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Emissions characterization during remote NF_3/O_2 chamber clean of silicon carbide

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EMISSIONS CHARACTERIZATION DURING REMOTE NF_3/O_2 CHAMBER CLEAN OF SILICON CARBIDE

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

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Abstract

The semiconductor industry uses multiple long-lived fluorinated gases for chemical vapor deposition chamber cleaning. These gases when emitted into atmosphere have an impact on the environment through global warming. The Environmental Protection Agency (EPA) and industry have instituted programs to measure and reduce perfluorocompond (PFC) emissions. One of the reduction strategies adopted is alternative technology.

This thesis presents the results of a research designed to optimize a Remote Plasma Source (RPS) clean process for silicon carbide film deposition. The best clean time was obtained for 700sccm NF_3/2300 sccm Ar/ 500sccm O_2/ 2.6Torr / 450W RF. NF_3 utilization efficiency was better than 98%. A fluorine mass balance of only 78% was achieved suggesting that some solids containing residues might have been formed. Increasing the clean time by 25% helps reducing the particle formation. A design of experiment around the optimized clean recipe was performed and the PFCs emissions modeled.

Acknowledgment

I would like to take this opportunity and thank the committee members for taking the time to read this thesis and their valuable comments. I am grateful to Dr. Gregory Young for his guidance and his patience in letting me work at my own pace on this research. I am extremely thankful to Dr. Sebastien Raoux for his support, help, and advices. I also appreciate Dr. Stacy Gleixner for her time and recommendations.

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GLOSSARY

Blok: Barrier Low k is a silicon carbide film used as interlayer dielectric for copper deposition.

CVD: Chemical Vapor Deposition is the formation of solid thin film on a substrate by the reaction of vapor phase chemicals that contain the required constituents.

DOE: Design of Experiment determines the fewest number of runs needed to gain adequate information for optimizing quality.

FTIR: Fourier Transform Infrared is an instrument that measures the interaction of matter with infrared radiation.

GWP: Global Warming Potential represents how much a given mass of a chemical contributes to global warming compared to the same mass of carbon dioxide.

JMP: Software for interactive statistical graphics. It is used to design experiments, edit spreadsheet, and analyze data.

Kg CE: Kilogram of Carbon Equivalent is a measure of the equivalent mass of CO_2 emitted into the atmosphere in kilograms.

MMTCE: Million Metric ton of Carbon Equivalent is a measure of the equivalent mass of CO_2 emitted into the atmosphere in million metric ton unit.

PFC: Perfluorocompounds include all molecules that contain carbon and fluorine plus NF_3 and SF_6.

Prob>t: The probability that the value estimated by the model is due to the chance alone. It is usually used to predict interactions between variables.

QMS: Quadrupole Mass Spectrometer is an analytical instrument that identifies ions by way of measuring their mass-to-charge ratio.

RF: Radio Frequency power.

RGA: residual Gas Analyzer is a mass spectrometer that identify ions by way of measuring their mass to charge ratio.

RPS: Remote Plasma Source is a high density plasma source usually located upstream of the film deposition reactor.

Rsquare: The proportion of variation explained by the model. The higher is R^2 value, the best is the model.

Standard deviation: It is the expected deviation of a random variable from its expected value. It is used to evaluate the experiment's error.

TFAA: Trifluoro Acetic Anhydride.

TMS: Tri Methyl Silane

Utilization efficiency: The percentage of the cleaning gas that was dissociated by the plasma.

Chapter 1

Introduction

1.1. Outline

To date, most of the focus on greenhouse gas emissions reduction opportunities in the U.S. has been related to carbon dioxide (CO_2) emissions. This is understandable since CO_2 emissions currently account for about 82 percent of the total U.S. greenhouse gas emissions weighted by 100-year global warming potentials (EPA, 1997). However, a number of recent analyses suggest that the non-CO_2 greenhouse gases, mainly perfluorocoumpounds (PFC), can make a significant contribution to emissions reductions. This research presents the results of a continuing study designed to reduce the global warming gas emissions from the semiconductor industry. The research focuses mainly on chemical vapor deposition (CVD) chamber cleaning because this process represents 50 to 70% of the total PFC emission in the semiconductor manufacturing (Raoux, 1999).

The first chapter of this report introduces the source and background of the global warming issue during the CVD chamber cleaning as well as the solutions adopted by the semiconductor manufacturers. Recently, Applied Materials has launched a new post-deposition cleaning method, which employs a remote plasma source (RPS) to yield minimum PFC emissions. The description of this technology is also presented in Chapter

One. The second chapter is a literature review related to the PFC reduction strategies in general and to the RPS technology in particular. The applicability of the RPS was extended to cleaning a silicon carbide film called Barrier Low K (Blok). Chapter Three introduces Blok film and talks about the purpose of this research. Chapter Four depicts the experimental methodology. Chapter Five describes the results and discussion. This section covers optimization of the chamber clean with different process parameters, a fluorine mass balance, and a fully developed design of experiment designed to model the PFCs emissions. Chapters Six and Seven cover the conclusion and future work respectively.

1.2. Background

During the plasma-enhanced chemical vapor deposition (PECVD) of thin films, deposition occurs not only on the substrate, but on all interior reactor surfaces. If not removed, these films accumulate, flake off and cause critical particulate problems during the PECVD process. Periodic cleaning is necessary. The frequency of the cleans depends on the nature of the film and thickness of the deposited layer (gas flow and deposition time).

Fluorocarbon in-situ plasmas are extensively used in the semiconductor industry to clean process chambers. The process consists of striking plasma in the reactor where a cleaning gas is introduced. Common feedstock gases employed are perfluoromethane (CF_4) and perfluoroethane (C_2F_6). The principal role of the plasma in the clean process is

to break the gas molecules into fluorine atoms and radicals. Fluorine radicals are very reactive; they effectively etch the residues and clean the chamber.

1.3. Global Warming Issue

The disadvantage of the in-situ plasma clean method using fluorocarbons is that partial decomposition of the perfluorocarbon molecule results in emissions products and unused reactants that when released untreated to the atmosphere have an environmental impact through global warming, generally referred to as the 'green house effect'. Each gas flowing into the reactor and each by-product produced in the plasma have their own unique global warming potential (GWP). PFCs are high GWP gases that are many times more effective than CO_2 in contributing to global warming. The GWP for a given gas depends on its atmospheric lifetime to destruction (by reaction or photodissociation), its infra red absorption coefficient and those of its atmospheric destruction by-products. For the perfluorocompounds of primary concern in the atmosphere, the GWPs are many thousands of times higher than the reference gas, CO_2, because of their extended lifetimes in the atmosphere and their larger infra red absorption coefficients. Table 1 reports the GWP100 (calculated over 100 years) and the GWP (calculated over an infinite time horizon) for different gases used as clean gas or as by-products of the PECVD chamber clean process.

Formula	Lifetime (years)	GWP (100 years)	GWP (infinite)
CO_2	50-200	1	1
CH_2F_2	5.6	650	
$C_3H_3F_5$	7.3	790	
C_3F_8	2600	7000	130,000
CF_4	50000	6300	850,000
C_4F_8	3200	8700	
CHF_3	250	12100	11,000
C_2F_6	10000	12500	230,000
C_3F_6	<1	Low	
NF_3	740	8000	18,000

Table 1. PFC Characteristics.

1.4. PFCs Reduction Strategies

The concern over the fate of atmospherically persistent PFCs has driven semiconductor manufacturers to seek out solutions that reduce global warming potential for plasma enhanced chemical vapor deposition chamber cleaning processes. In 1996, the Environmental Protection Agency (EPA) began implementing emission reduction partnership for the semiconductor industry. This is a voluntary partnership with U.S. semiconductor producers with the goal of developing ways to reduce the emissions of high global warming potential gases used in semiconductor manufacturing. Opportunities to reduce emissions from CVD cleaning emissions fall into the following five categories:

- **Alternative chemicals.** Consists of substituting the PFCs with gases that have lower GWPs and lower atmospheric lifetimes. It has been shown that these substitutes may have faster or comparable etching rates, increased etching efficiency, and may lead to an overall reduction in the amount of PFCs (Sun *et al.* , 1998)
- **Abatement systems.** This solution consists on reducing the amount of undesirable species emitted into the atmosphere by destroying unreacted PFC molecules by means of plasma abatement, thermal destruction, or catalytic destruction. The plasma system dissociates PFC molecules, which reacts with an additive gas such as H_2, O_2, H_2O, or CH_4 in order to produce low molecular weight by-products such as HF with no GWP. Wet scrubbers can then remove these product molecules. The thermal destruction is a fuel combustion process that destroys PFC molecules but produces emissions of NOx which are regulated air pollutants. The catalytic destruction process

consists of reducing the GWP gas emissions by means of reaction of the PFCs with water at high temperature (~700^0 C) in the presence of a catalyst. The byproducts formed are mainly HF and CO_2, in-house scrubbers then remove HF.

- **PFC recapture/recovery.** This technology separates unreacted and process-generated PFCs from other gases for further processing. This effluent treatment process allows for the possibility of some recycling or reuse of the captured PFC gas (Mocella, 1998). These systems can either repurify the PFC for reuse or they can concentrate the gas for subsequent offsite disposal. This technology is unattractive if NF_3 cleaning systems are used because such cleaning processes do not leave sufficient PFC in the stream to make gas recovery economically viable.
- **Process optimization.** This practice involves the use of end-point detectors and process parameter variations to find the minimum level of PFC utilization to reduce excess emissions.
- **Alternative process technology.** This strategy requires a radical modification of the process, gas and hardware, in order to eliminate the PFCs emissions and improve the clean process performance. Applied Materials has launched a new process technology which employs remote plasma source (RPS) to yield minimum PFC emissions. The description of the RPS is detailed in the next section of this Chapter.

1.5. Remote Clean Technology

1.5.1. Concept

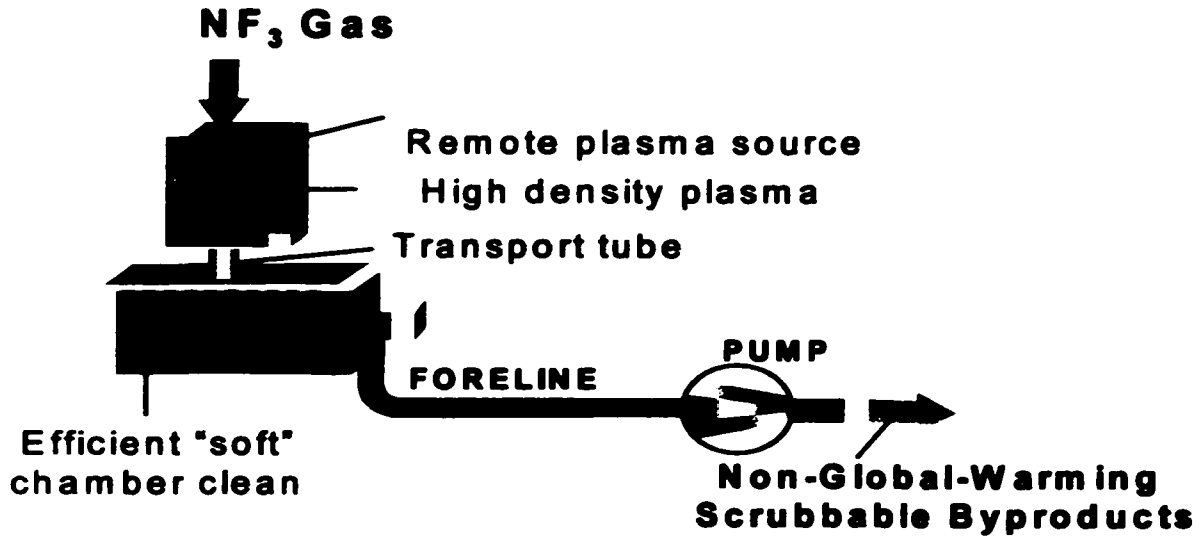


Figure 1.1. Remote plasma technology.

The Remote Clean™ involves generation of a high-density plasma source upstream from the processing chamber (Figure 1.1*)*. A typical feedstock gas used in this process is NF_3. The plasma almost completely dissociates the gas to fluorine and nitrogen atoms and molecules (>95% dissociation). Reactant products are "injected" in the process chamber to dry etch the residues deposited on the chamber walls. The plasma source is limited to the region inside the applicator, therefore, the clean process inside the chamber is driven only by chemical reaction unlike in-situ plasma clean that is driven by ion

energy. The advantage of producing the plasma in an antechamber is that the deposition equipment is not subjected to the energetic ions, electrons, and photons inherent to highly energetic plasmas. Therefore, this technology improves the lifetime of the chamber hardware.

The remote plasma source (RPS) consists of a compact lid-mounted toroidal plasma source. The remote unit utilizes a low field toroidal plasma to effectively dissociate NF_3. Inside the RPS, the power is coupled through a primary winding on a donut shaped ferrite core, which is inter-looped by a plasma acting as a secondary. The primary coil is powered by a 400 kHz switching power supply that can provide up to 5 kW of power, depending on the operating conditions. A dilution of NF_3 by Argon is required in order to strike and sustain the plasma. A schematic of the remote is shown in Figure 1.2.

1.5.2. NF_3 Feedstock

The choice of the clean gas is important in this process. The advantage of NF_3 over perfluorocarbon etchers is the weaker nitrogen-fluorine bond as compared to the carbon-fluorine bonds (Raoux. 1999). Table 2 shows comparative bond strength of NF_3, NF_2, CF_4, and C_2F_6.

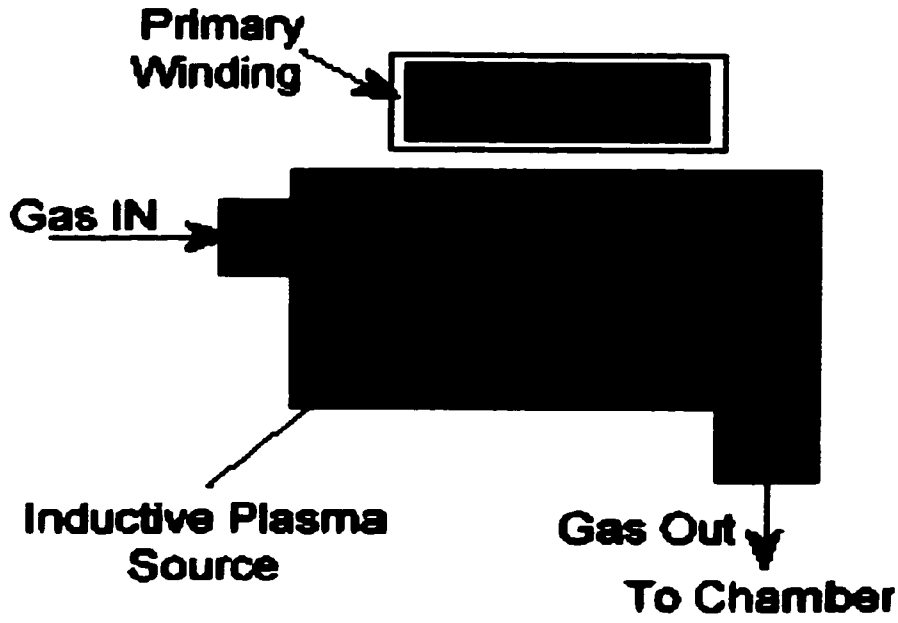


Figure 1.2. Schematic of the remote plasma source. (Raoux, CET)

Source	Products	Bond Strength (kcal/mole)
NF_3	$NF_2 + F$	59
NF_2	$NF + F$	58
CF_4	$CF_3 + F$	130
$C2F_6$	$C_2F_5 + F$	127

Table 2. Comparison of N-F and C-F bond strengths for common PFC gases

NF_3 low bond strength makes its destruction relatively easy, combined with the lack of significant removal recombination, results in an efficient source of fluorine radicals. NF_3 remote technology has the unique ability to provide an effective source of fluorine resulting in a good clean rate, better etch rate and clean environment. However, due to recombination of fluorine atoms to fluorine molecules, the remote clean technology generates large quantities of F_2, which must be scrubbed by an appropriate technique to prevent fluorine emissions into the atmosphere.

Chapter 2

Literature Review

2.1. PFC Reduction

To reduce the emission of PFCs, alternative chemicals and optimization are usually given the highest preferences because of their potential to solve, rather than mitigate, the emissions problem. Most of the studies that deal with the PFC emissions in the semiconductor industry evaluate the process from an environmental and performance standpoint. An optimum solution is one that can reduce the emissions and increase the performance of the hardware without increasing the cost of the process.

In order to estimate the PFC emissions from a clean process, the MMTCE (Million Metric Ton Carbon Equivalent) has to be evaluated. The MMTCE is a measure of the equivalent mass of CO_2 emitted into the atmosphere. The MMTCE values allow the comparison of different clean processes. If Q is the mass of the emitted gas and 12/44 is the ratio of the carbon to carbon dioxide molecular weights, the MMTCE can be expressed as:

$$\underset{(10^6\ \text{Ton})}{MMTCE} = \frac{Q_{(kg)} \times (12/44) \times GWP}{10^9} \qquad (1)$$

Sun et al. (1998) investigated the chemical vapor deposition (CVD) chamber clean using C_3F_8/O_2 in situ plasma as an alternative to the conventional C_2F_6 plasma clean. He found that 60 to 70 % reduction in PFC emissions can be achieved, this was due to the fact that C_3F_8 has a lower global warming potential and a lower lifetime in the atmosphere than C_2F_6. Pruette et al. evaluated the environmental performance of trifluoroacetic anhydride (TFAA) as alternative to C_2F_6 and to C_3F_8 (Pruette, 1998). The PFC emissions were reduced by a factor of 25 over C_2F_6 clean, and by a factor of 8 over a standard C_3F_8. When the remote clean technology was introduced, Raoux et al. found that NF_3 remote plasma could "virtually" eliminate the PFC emissions (Raoux 1999).

2.2. Process Performance

Sun investigated the process performance when C_3F_8/O_2 mixture was used to clean the chamber. A design of experiment (DOE) was performed to model the effect of the cleaning gas flow and the reactor pressure on the clean time. It showed that the pressure caused the major change in the etch time followed by C_3F_8 flow. When holding the O_2 flow constant, the clean time decreases with increasing C_3F_8 flow. However, increasing O_2 and C_3F_8 flows has an inverse effect on the clean time. Sun concluded that a C_3F_8: O2 ratio less than 1 is required for an optimized etch process clean time. C_3F_8 usage slightly improves the clean time (6%), but considerably improves the clean gas utilization from 24-35% for C_2F_6 to 63-71% using C_3F_8.

When the process performance was evaluated using trifluoroacetic anhydride (TFAA) as an alternative chamber clean gas on a plasma enhanced chemical vapor deposition, Pruette et al. found that the TFAA clean time was 20% faster than C_2F_6 clean times. A central composite DOE with three center point replicates was performed to examine the effect of chamber pressure, TFAA gas flow, and O_2 gas flow on the reactor clean time and TFAA utilization efficiency. The utilization efficiency, also called the destruction efficiency, is the percentage of the cleaning gas volumetric flow that is dissociated by the plasma. It is defined by the equation below:

$$\% \text{ Utilization} = 100 * \{ 1 - (\text{Flow of clean gas in (scc)} / \text{Flow of clean gas out (scc)})\} \quad (2)$$

Of the three parameters studied, the least variation occurred in TFAA utilization efficiency; 97% or more of TFAA was destroyed in the plasma in most of the cases, except when the chamber pressure was relatively high.

Raoux et al. (1999) investigated the process performance when the RPS with NF_3 was used as alternative to the fluorocarbon in-situ plasma. It was found that in all cases the utilization efficiency of the gas was higher than 90%. Other fluorocarbon gases especially CF_4 are very stable molecules that are hard to break apart, and higher power density, gas residence time, and gas flow are required to obtain an equivalent destruction efficiency. When the process stability was studied, Raoux found that excellent process repeatability was obtained over thousands of processed wafers; the use of the remote clean did not have an impact on the chamber hardware due to the absence of ion

bombardment. Figure 2.1 a/b shows the chamber surface after 150 hours using in-situ NF_3 and NF_3 remote clean. Figure a shows that the surface metal was degrading with a buildup of a film of aluminum fluoride when the plasma was used inside the chamber. When the remote clean was used, no film buildup or hardware damage was apparent in the chamber as shown in Figure b.

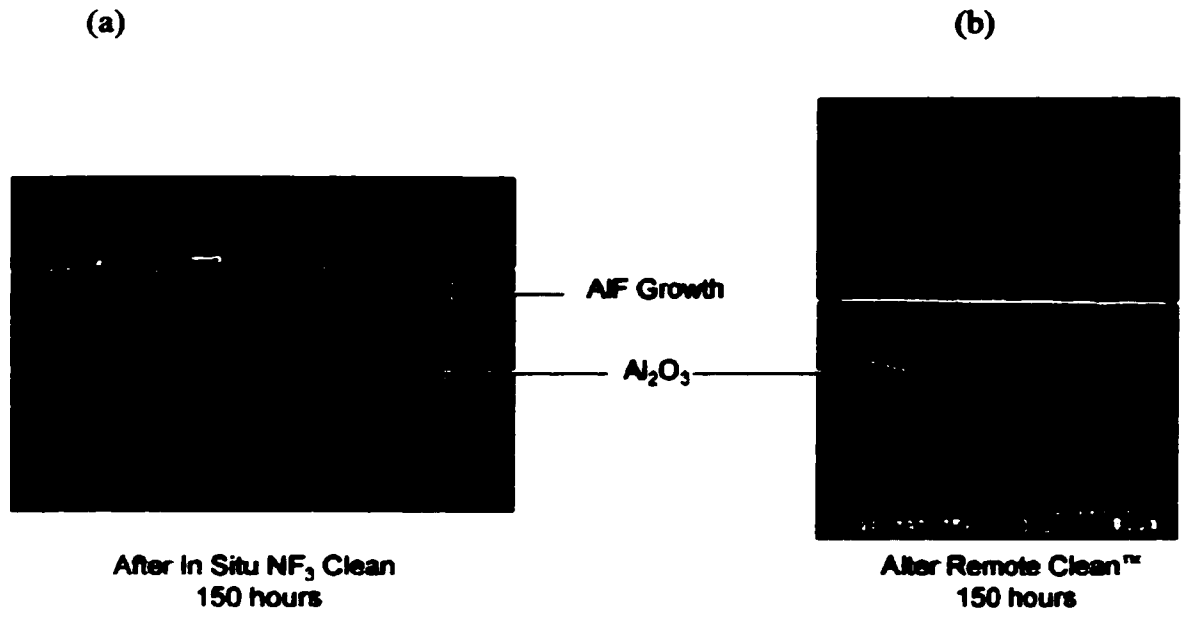


Figure 2.1. Hardware stability, active in-situ plasma versus remote clean

Raoux found also that when the remote plasma was compared to in situ plasma clean (CF_4 or C_2F_6 based cleans), the clean time was reduced by 55 to 61% for silicon nitride and silicate glass, and by 28% for silicon oxide.

2.3. Cost Analysis

The EPA has performed a cost analysis in order to estimate the costs of implementing the PFCs reduction technologies (EPA, 2000). Cost analysis were conducted for NF_3 RPS technology, plasma abatement, thermal and catalytic destruction, and recapture/recovery technologies. Process optimization and lower GWP substitutes were not considered due to the lack of test data. The analyses were based on the assumption that the U.S. semiconductor fabrication facilities (fabs) use between 75,000 to 150,000 pounds of PFC per year of which 60 to 80% of PFCs are emitted. The total annual costs for implementing NF_3 RPS is $95,000 per fab, which includes capital, operations, and maintenance costs. Emissions reductions are estimated to be 5,500 metric tons of carbon equivalent (TCE). The RPS uses approximately 1,400 pounds of NF_3/year. The C_2F_6 in-situ clean would require 5 times this amount or 7,000 pounds per year. The cost of emission reductions using RPS is therefore estimated to be $17 per TCE (EPA, 2000). Similarly, the costs of emission reductions using the other technologies are: $38 per TCE for the plasma abatement, $111 per TCE for thermal destruction system, $102 per TCE for catalytic destruction, and $36 per TCE for recapture systems.

2.4. Literature Review Summary

The major conclusion from this literature review is that the use of alternative chemicals to reduce PFC gases emissions offers the advantage that little or no changes are required of the existing processes. However, the long-term viability and economic impact of the alternative gas are unclear. The PFCs are reduced but no significant amelioration of the process performance is achieved. On the other hand, the NF_3 remote technology has the advantage that it virtually eliminates PFC emissions, improves the tool productivity, and lowers the cost of consumables (soft clean without ion bombardment). The remote technology is also cheaper to implement as compared to the abatement or recycling systems. However, the total destruction of NF_3 produces large amount of fluorine. For films such as silicon nitride and silicon oxide, the fluorine does not have a significant effect on creating other PFCs, but for films that have large amounts of carbon such as silicon carbide, other PFCs could be formed; the effectiveness of the remote plasma in cleaning such films is also unknown. It is therefore, essential to characterize and optimize such processes.

Chapter 3

Purpose of Study

3.1. Blok Process

The purpose of this research is to extend the applicability of the remote clean to a new process called Blok (Barrier Low K). Blok was introduced as interlayer dielectric (ILD) that is used after each copper deposition on the wafer to provide a barrier against copper diffusion, moisture, and impurities. This silicon carbide provides an alternative to silicon nitride films, enabling chipmakers to reduce the dielectric constant (k) and therefore to achieve faster and more powerful devices. Blok film is composed of silicon, carbon, and hydrogen. It has a low dielectric constant and high dielectric strength. The dielectric strength of a material is measured by the maximum voltage the material can withstand without breakdown. The dielectric constant k is a measure of the material's ability to store electric charge.

Characterization of the clean process was performed with the goal of evaluating the environmental performance as well as the process performance of the remote clean. Mass Spectroscopy (MS) and Fourier Transform Infrared Spectrometry (FTIR) methods were used. The application of these analysis methods provide quantitative information on the process behavior, clean end point, clean rate, plasma behavior, and PFC emissions.

3.2. Motivation

The use of NF_3 remote clean is efficient in cleaning films such as silicon dioxide or silicon nitride, but the performance of the method in cleaning silicon carbide residues is unknown. One specific concern of etching Blok film is to remove the carbon from the $Si_xC_yH_z$ residues. Using pure NF_3 chemistry, this can be done by forming CF_4 as a byproduct which is a high GWP PFC gas. To avoid CF_4 formation, it is necessary to add oxygen to the discharge. In this case, CO, CO_2 and COF_2 are formed as additional byproducts. Of other concern is the addition of in-situ RF power to enhance the clean rate. It was shown that this RF power is necessary, especially for carbon-containing films, but can be damaging to the chamber hardware if too much power is applied (Emissions Measurements and Technology Database, 1999). A characterization of the clean process is therefore essential to ascertain the performance of the tool from emissions point of view and to optimize the process.

Chapter 4

Experiment Methodology

4.1. Process Description

The viability of utilizing the remote plasma as an alternative chamber clean is evaluated by measuring clean time and process emissions as a function of NF_3 flow, O_2 flow, chamber pressure, and radio frequency (RF) power in the chamber. The RPS process is studied by cleaning a 500 Å PECVD of silicon carbide on a 200 mm wafer. The deposition process uses trimethylsilane (TMS), diluted with helium, as deposition precursor.

After each deposition, the wafer is removed from the reactor and the cleaning process is performed in order to remove the residues from the chamber walls and showerhead. The cleaning process uses an NF_3/O_2 / Ar gas mixture. This mixture is dissociated in a remote plasma source placed upstream of the PECVD reactor. The fluorine ions produced by dissociation of NF_3 are diffused into the reactor where they dry etch the silicon carbide residues in the wall and surface chamber. An additional RF power is applied in the chamber in order to dissociate the recombined fluorine molecules. The residues are converted to silicon tetrafluoride (SiF_4) and various chemical byproducts. A schematic of the clean process is displayed in Figure 4.1. The process emissions are removed from the chamber by a dry vacuum pump where they are mixed with pump

dilution gas (N_2) and then sent to the acid exhaust system and water scrubber. Corrosive emissions and particulate byproducts are removed by scrubbing with water. Perfluorocompounds are more stable, they not removed by the wet scrubbers and are emitted into the atmosphere.

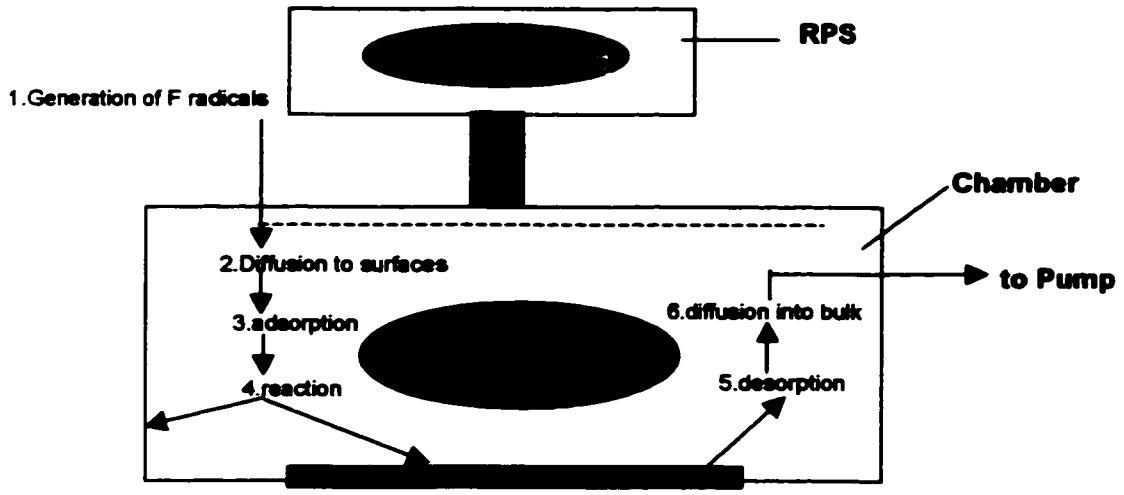


Figure 4.1. Schematic of the Cleaning Process.

$$F^{\cdot} + C_xH_ySi_z + O_2 \longrightarrow CF_4 + COF_2 + SiF_4 + \text{Other Byproducts}$$

4.2. Emission measurement and Technology

4.2.1. Experimental Set-up

The measurements are performed after the chamber exhaust pump. A fraction (1 to 5%) of the stream is drawn to be analyzed and quantified using a quadrupole mass spectrometer (QMS) in parallel with a Fourier transform infrared (FTIR). In order to monitor the process in real time, another mass spectrometer, also called residual gas analyzer (RGA), is hooked up directly in the chamber. The RGA is not used for quantitative measurements of the gases, but only used to monitor the beginning and ending of the clean time (end point detection). A schematic of the experimental setup is shown in Figure 4.2. The quantitative analytical instruments are located in approximately 4 feet from the process pump exhaust. The instruments sample the gases through $1/8^{th}$ inch diameter stainless steel tube that is heated to 115 ^{0}C to eliminate the water vapor from the line. The pressure in the sampling line is adjusted with a needle valve and maintained at 740 Torr throughout the experiment.

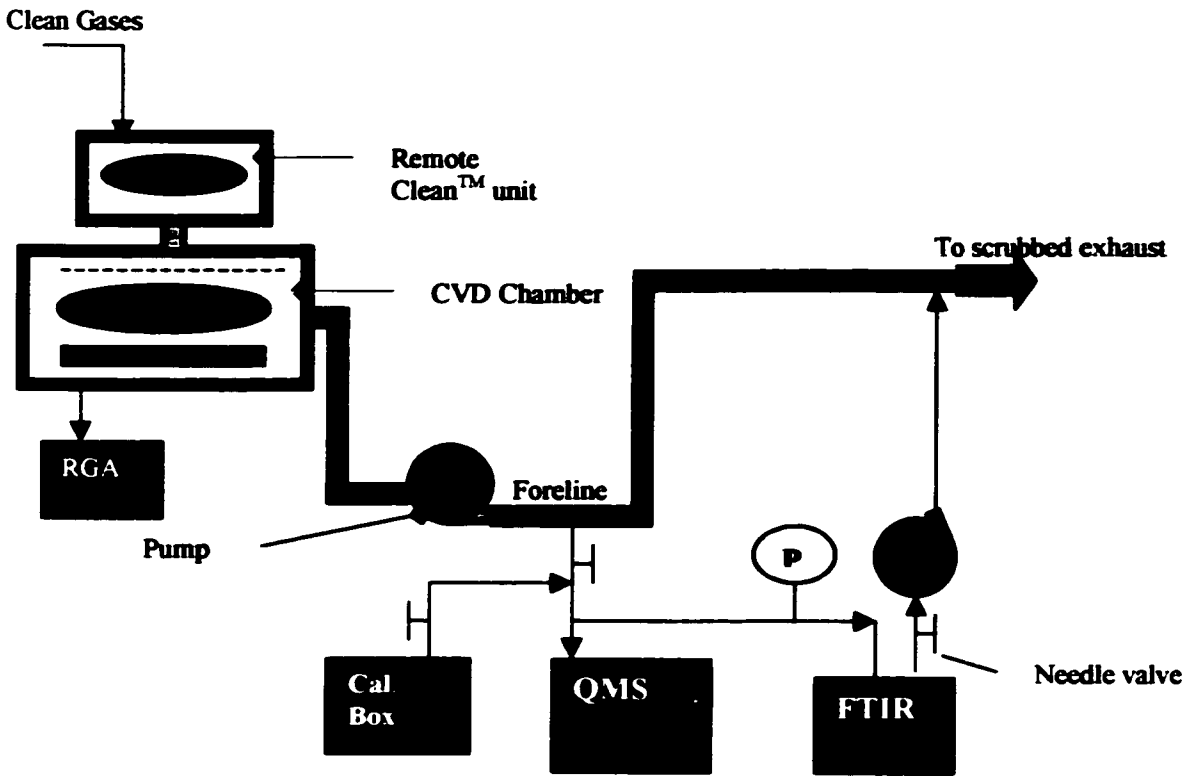


Figure 4.2: Schematic of Experimental Setup.

4.2.2. Analytical Instruments and Methodology

- ***Quadrupole Mass Spectrometer***

The clean processes are monitored with a UTI QMS analyzer having a 200 atomic mass unit (AMU) filter. This instrument is designed to sample a representative fraction of the process gas at atmospheric pressure. The flow of the gas sample is accomplished by successive reduction of pressure from the process through the compound pump through fixed geometry pump-in channels. The total pressure in the QMS is adjusted to 10^{-6} Torr by adjusting the electron multiplier voltage. Analyses are accomplished in static mode (0-200 AMU) and in selected peaks mode (up to 10 monitored ion species). The response time of the QMS (time between the beginning of injection of the gas in the process chamber and the detection in the QMS) is less than 25 seconds. (Refer to Appendix A for a detailed QMS theoretical description.)

- ***Fourier Transform Infrared Spectroscopy***

The QMS has a limitation in quantifying all the byproducts of the clean process. Gases that have the same AMU, (Example HF and Ar with AMU 20), are difficult to monitor. To avoid deconvolution of interfering peaks and to minimize the errors, FTIR measurements are performed using a Nicolet Nexus™ spectrometer with a 5 cm gas cell. The FTIR spectral series are recorded with an 8 cm^{-1} resolution with each spectrum being an average of 16 scans. (Refer to Appendix B for an FTIR theoretical description.)

- ***Calibrations***

The instrument calibrations are performed after each experiment using a dynamic calibration system. The gas source is a regulated gas cabinet where lecture bottles of calibration gas standards are placed. The lecture bottles contain a high pressure (~1500 psi) dilute (1%) mixture of the compound of interest in a balance of nitrogen. This system has two mass flow controllers (MFCs), one is used to regulate the amount of standard gas and the other is used to further dilute the gas with high purity nitrogen. Dilution by a factor of 1 to 500 may be achieved in this way. A preliminary listing of the components that are monitored and calibrated during this study is shown in Table 3.

Species	CF4	COF2	SiF_4	NF_3	F_2	HF
IR region (cm^{-1})		-	-	-	-	~4038
QMS(AMU)	69	47	85	52	38	
Quant. method	QMS	QMS	QMS	QMS	QMS	FTIR

Table 3. Effluent Species and Detection Methodology

- ***Pump Purge***

During this study, the measurements are made downstream of the process pump. To avoid reaction and corrosion of the pump and foreline, the process byproducts are diluted with the nitrogen before entering the pump. To determine the actual volumetric

emissions, it is necessary to calculate the pump purge dilution factor. The pump purge is determined by flowing NF_3 gas from the CVD tool, without igniting the plasma, at different flow rates (from 0.5 to 0.05 liter/minute) and then by measuring its concentration using the QMS which had been previously calibrated for NF_3. The pump purge is determined by the equation below (Equipment Environmental Characterization Guidelines, Rev.3.0):

$$N_{2\,pumppurge_{slm}} = \frac{NF_{3_{slm}} \times 10^6}{[NF_3]_{ppm}} - NF_{3_{slm}} \qquad (3)$$

Where NF_{3slm} is the volumetric flow of NF_3 in standard liter per minute, $[NF_{3ppm}]$ is the concentration of NF_3 in part per million.

After accurately measuring the pump purge flow rate with the calibration gas, the concentrations measured for various compounds can be converted to flowrates specified in sccm.

4.3. Experimental Plan

The characterization of the RPS for a Blok film starts by developing a clean recipe and looking at the corresponding clean time. This will be performed by varying the process parameters one at a time with the assumption that there are no interactions between the parameters. The second step consists of performing a fluorine mass balance with the "optimized" clean time and evaluating the condition of the chamber (formation of particles). The third and final step is to optimize the PFC emissions by design of experiment around the optimized recipe. A flow chart of the experimental plan is shown in Figure 4.3.

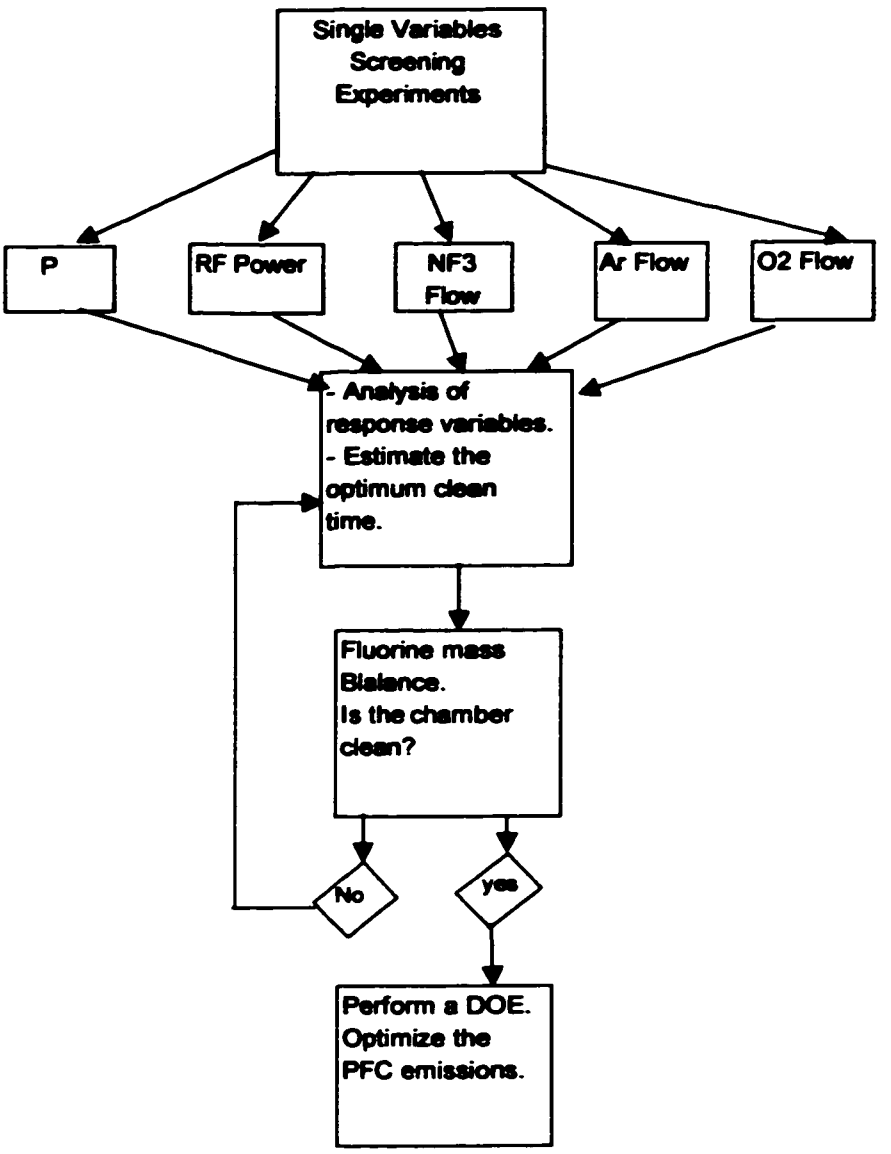


Figure 4.3. Flow Diagram of the Experimental Plan.

4.3.1. Screening Experiments

Screening experiments are necessary at the start of this study to determine the effect of process parameters (NF_3/O_2 flows, RF power, Argon flow and chamber pressure) on the chamber cleaning time and byproducts emissions. The results of the screening test are used to optimize the clean time and to define a center point around which a design of experiment (DOE) will be performed and the PFCs emissions will be determined. The screening test consists of changing one process variable at a time and keeping the other process variables constant. Table 4 shows the table matrix for the screening experiment.

	Clean#	NF3 (sccm)	Ar (sccm)	O2 (sccm)	RF (Watt	P (Torr)
NF3/Ar Flows	1	700	2300	500	450	2.65
	2	700	1000	500	450	2.03
	3	700	500	500	450	1.77
	4	500	2300	500	450	2.49
	5	500	1000	500	450	1.85
	6	500	500	500	450	1.58
	7	300	2300	500	450	2.29
	8	300	1000	500	450	1.66
	9	300	500	500	450	1.39
P	10	700	2300	300	450	2.6
	11	700	2300	300	450	3.5
	12	700	2300	300	450	5
O2 Flow	13	700	2300	100	450	2.6
	14	700	2300	200	450	2.6
	15	700	2300	300	450	2.6
	16	700	2300	400	450	2.6
	17	700	2300	500	450	2.6
RF Power	18	700	2300	300	1000	2.6
	19	700	2300	300	450	2.6
	20	700	2300	300	200	2.6
	21	700	2300	300	100	2.6
	22	700	2300	300	0	2.6

Table 4. Screening Experiment Matrix Table.

4.3.2. Mass Balance

Once the center point is determined from the screening test, a mass balance on fluorine is performed in order to estimate the utilization efficiency of NF_3 in the remote plasma and to quantify the perfluorocompounds emitted from the CVD chamber. The destruction efficiency is calculated using equation (2) from section 2.2.

The mass balance on fluorine is determined by balancing the number of fluorine equivalents injected into the remote clean against the number of byproduct fluorine containing gases measured at the exhaust of the pump:

Fluorine equivalent into the tool = (clean time)* 3* $[NF_3]_{sccm}$, the number three corresponds to the stoichometric balance of fluorine in NF_3 gas.

If the only perfluorocompounds detected are CF_4, F_2, COF_2, SiF_4, and unreacted NF_3, then:

Fluorine equivalent after the plasma = $4[CF_4] + 2[F_2] + 2[COF_2] + 4[SiF_4] + 3[NF_3]$

$$\text{Mass Balance on F} = \frac{\text{Fluorine Equivalent after the Plasma (exiting)}}{\text{Fluorine Equivalent in the Tool (entering)}} \quad (4)$$

The most challenging aspect of the emission measurement is the need to meet a 90% fluorine mass balance as required by the industry protocol (Equipment Environmental Characterization Guidelines, Rev. 3.0). This criterion requires all fluorine-containing byproducts to be identified and quantified requiring a calibration standard for every byproduct. A plausible explanation should be given if the fluorine mass balance did not close to 90%.

4.3.3. Design of Experiment

To estimate the effects of several variables simultaneously on the PFCs emissions, a response surface design of experiment around the center point will be performed. The response surface method will help to have an answer to how the process variables (RF power, pressure, O_2 flow, and NF_3 flow) affect the PFC emissions and what settings of variables will yield minimum emissions.

The matrix design of experiment is generated using Box-Behnken surface response design. The design table, as well as the analysis, is generated using a JMP software. The Box-Behnken design selected for four effects generates the design table of 27 runs. The response surface design selection dialog is shown in Figure 4.4.

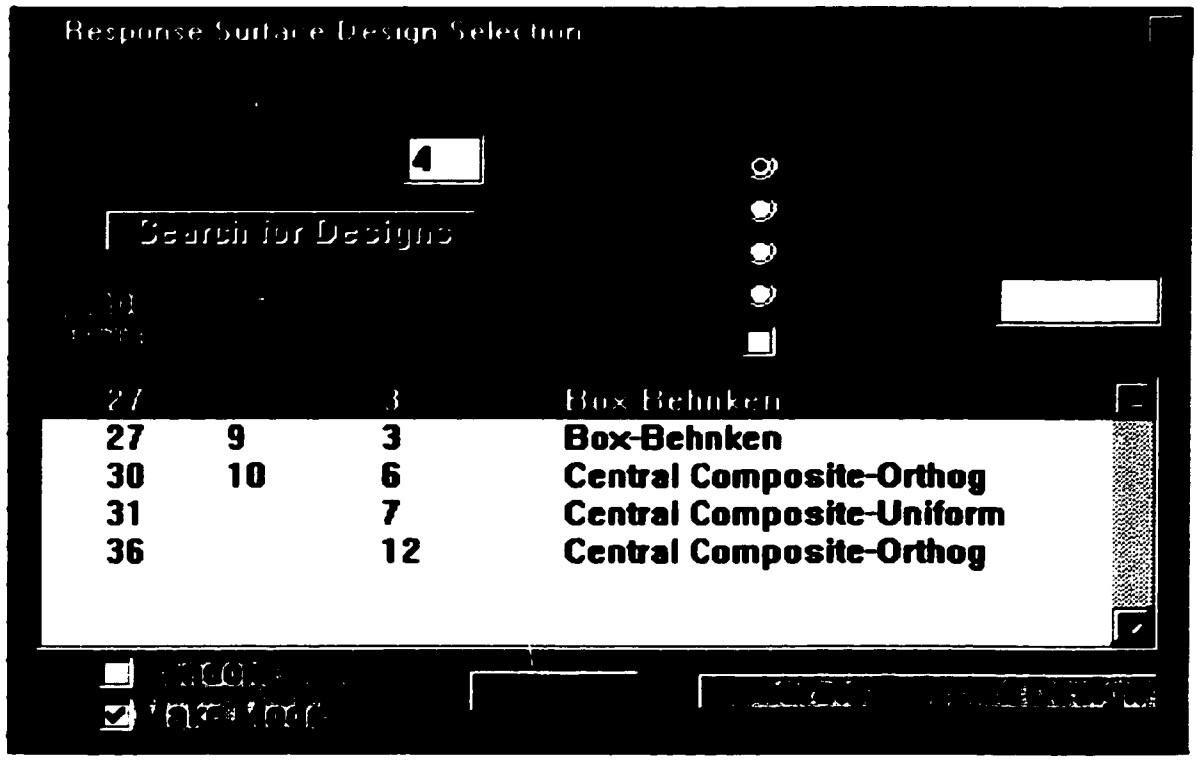


Figure 4.4. Response Surface Design Selection Dialog.

4.3.4. Error Estimation

The errors associated with this study can be attributed to measurements and to sampling. The errors of the measurements are calculated using the standard deviation (2 sigma). For the mass balance experiment, the clean recipe is run five times from which an average of the gases emissions measurements was determined as well as the standard deviation. For the screening experiment and the DOE, only the baseline recipe is run three times and the errors calculated during these runs are assumed to be equal to the other recipes errors. The errors contributing to the sampling instruments are estimated to be 7%. This error estimate includes 5% errors of the gas standards, 1% error of the MFCs, and 1% error of the inlet pressure (Ketkar, 1994).

Chapter 5

RESULTS AND DISCUSSION

5.1. Clean time optimization

Screening experiments are necessary at the start of this study to determine the effect of process parameters (NF_3/O_2 flows, RF power, Argon flow and chamber pressure) on the chamber cleaning time and byproducts emissions. The results of the screening tests are used to define a center point around which the best clean time is determined. The screening test consists of changing one process variable at a time.

5.1.1. Endpoint Detection

The major byproduct formed when a silicon-based film is etched with fluorine atoms is SiF_4. The basis of endpoint detection, and therefore the clean time, is the rate of SiF_4 evolution during the etching process. The different compounds of silicon react with the etch gas (fluorine) to form SiF_4. The rate of SiF_4 formation depends on the process parameters. The clean time is determined by monitoring SiF_4 at 85 atomic mass unit (AMU) using the RGA.

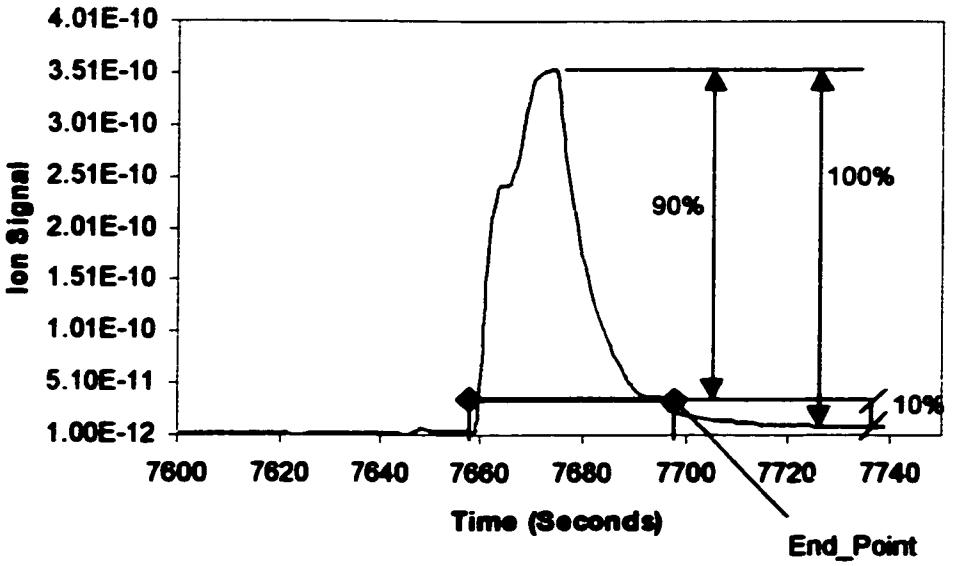


Figure 5.1. End-Point Detection

The end-point detection is very delicate to measure in a consistent manner. During this research, the method used for end point-detection is shown in Figure 5.1. This method consists of defining the clean time as the segment between the time when SiF_4 signal starts to increase and the time when the slope of the signal drops to zero which corresponds to 10% of the noise level.

5.1.2. NF_3 and Argon Flows Effects on Clean Time

One concern of the remote clean is the amount of NF_3 required in the baseline clean. Not only is NF_3 a costly gas, but a significant amount of fluorine is generated as a byproduct of the clean. To determine if an effective clean could be achieved with reduced

total NF_3 requirement, argon is added as a diluting gas in hopes that some amount of argon can maintain distribution of the free fluorine throughout the chamber. In this study the flow of argon was varied with different NF_3 flows.

The effect of NF_3 flow with a constant O_2 flow and RF power is depicted in Figure 5.2. As expected the clean time decreases with increasing NF_3 flow due to higher fluorine radicals injected into the chamber. The clean time is even lower when NF_3 is diluted with Ar. Addition of Ar flows helps stabilizing the plasma and reduces the fluorine recombination. The lowest clean time, 40 seconds, was achieved at 700 sccm and 2300 sccm flows of NF_3 and Ar respectively. 2300 sccm of Ar is the maximum flow available in the system. At these conditions an RPS power of 4.2 kW was needed to completely dissociate NF_3 gas. Table 5 shows the clean time measured during this experiment.

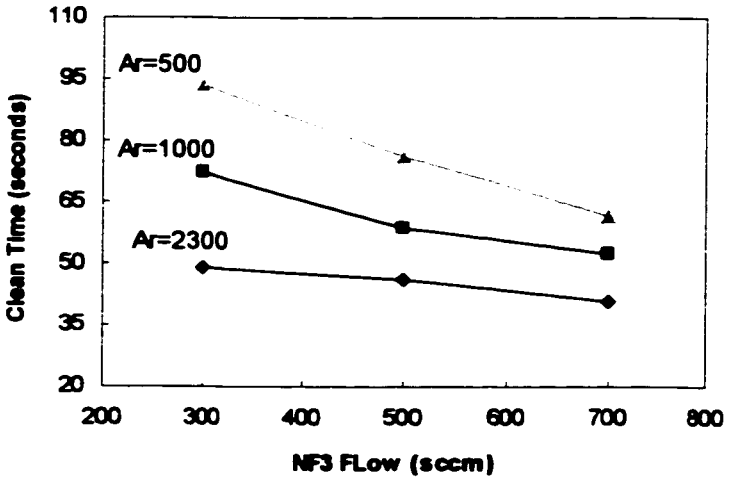


Figure 5.2. Effect of NF_3 and Ar Flows on the Clean Time.

Clean#	NF3	Ar	Clean Time
1	700	2300	40.6
2	700	1000	52.2
3	700	500	61.6
4	500	2300	46
5	500	1000	58.5
6	500	500	76
7	300	2300	49.1
8	300	1000	72.3
9	300	500	93.75

Table 5. NF_3 and Ar Flows Effect on Clean Time.

5.1.2. In-situ RF Power Effect on Clean Time

The in-situ RF power was varied from 0 to 1000 watts while other process parameters were kept constant. In general, the clean time decreases with RF power except in the region 0-100 where the clean time was increasing. The mechanism in this region is unclear, but the increase in clean time can be attributed to the noise since the experiment's errors based on 2σ standard deviation were estimated to 3.2 seconds.

Figure 5.3 and Table 6 show that an RF power increase from 450 W To 1000 W improves the clean time by only 5 seconds. An RF power of 1000 W would increase the ion bombardment and damage the chamber, therefore, 450 Watt seems to provide the best compromise.

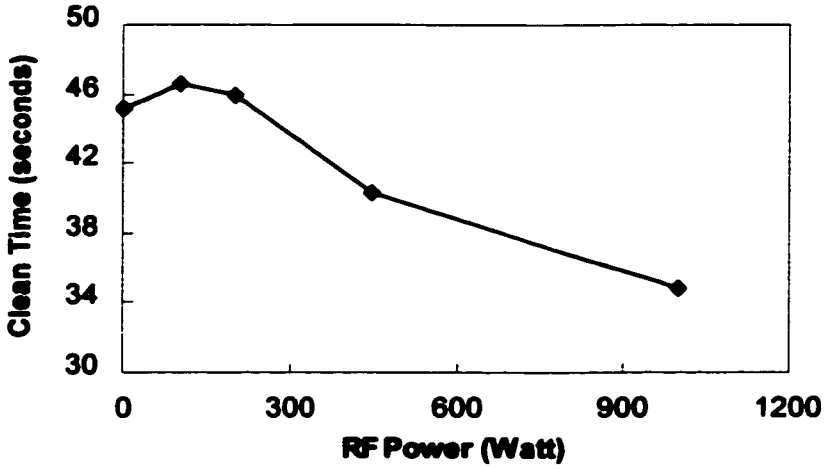


Figure 5.3. Effect of in-situ RF Power on the Clean Time.

Clean #	RF	Clean Time
18	1000	34.9
19	450	40.3
20	200	45.9
21	100	46.6
22	0	45.2

Table 6. RF Power Effect on Clean Time.

5.1.3. O_2 Flow Effect on Clean Time

The third parameter that was evaluated is the oxygen flow. Additional flow of O_2 was necessary to clean the chamber from carbon residues. Figure 5.4 and Table 7 show that increasing O_2/NF_3 ratio helps improving the clean time. An O_2 flow of 500 sccm was estimated sufficient to enhance the chamber clean.

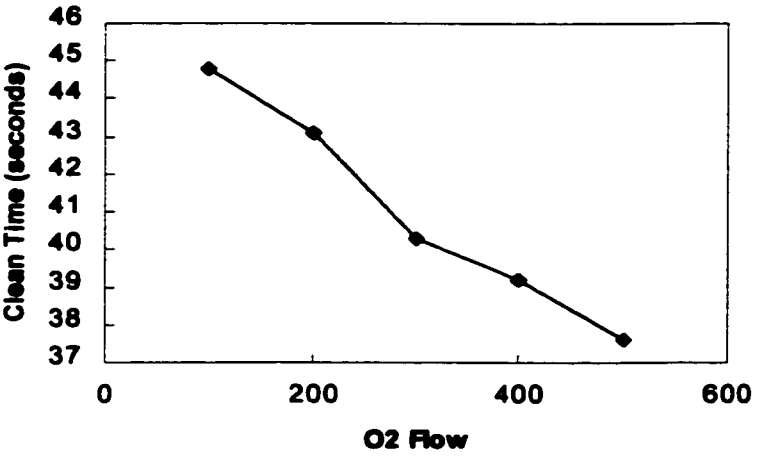


Figure 5.4. Effect of O_2 Flow on the Clean Time.

Clean #	O2	NF3	O2/NF3	Clean Time
13	100	700	0.14	44.8
14	200	700	0.29	43.1
15	300	700	0.43	40.3
16	400	700	0.57	39.2
17	500	700	0.71	37.6

Table 7. O_2 Flow Effect on Clean Time.

Oxygen reacts with carbon residues to form CO_2 and other fluorine containing compounds such as COF_2. Figure 5.5 depicts the selectivity of O_2 to form COF_2, which is not a global warming gas, over CF_4, which is a high GWP gas. It should be noted that too much oxygen can reduce the power available to NF_3 and increase the chamber pressure.

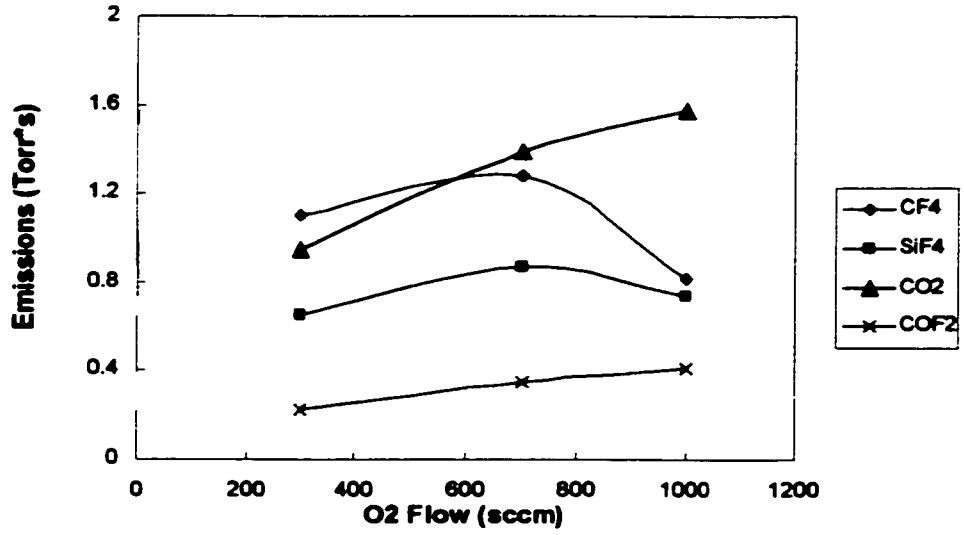


Figure 5.5. Effect of O_2 and NF_3 Flows on the emissions.

5.1.4. Chamber's Pressure Effect on Clean Time

The effect of the pressure on the clean time was moderate compared to the effect of NF_3 and Ar flows. Figure 5.6 indicates clearly that the chamber clean is faster at lower pressure. This is because at lower pressure the mean free path of the energetic free F radicals is longer. At higher chamber pressure the collisions between F radicals is causing them to recombine and hence making longer clean time. The clean time increased from 40 to 50 seconds when the pressure varied from 2.6 to 5 Torr. A pressure of 2.6 Torr was the lowest pressure reached in the chamber for 700/2300/500 sccm of $NF_3/Ar/O_2$ flows. Table 8 depicts the variation of the clean time with the pressure.

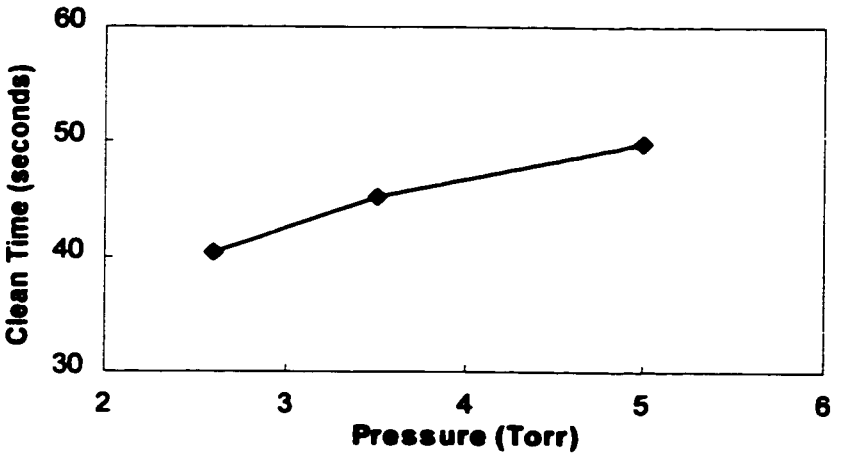


Figure 5.6. Effect of Chamber Pressure on the Clean Time.

Clean#	P	Clean Time
10	2.6	40.3
11	3.5	45.2
12	5	49.8

Table 8. Pressure Effect on Clean Time.

5.1.5. JMP Model

JMP is software for interactive statistical graphics. It is used to design experiments, to edit spreadsheet, and to manipulate and analyze data. The complete data tables for single variable experiment was entered into JMP.

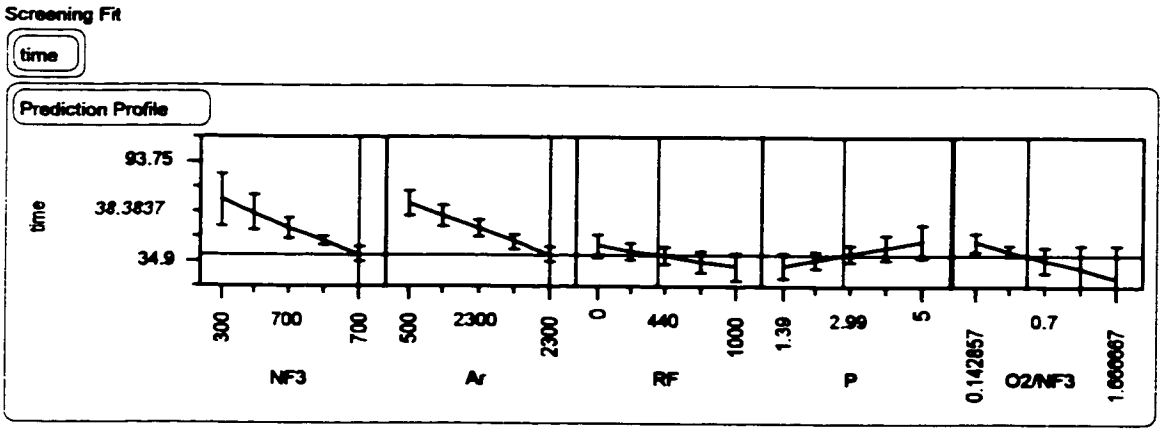


Figure 5.7. Single variable effect on the clean time.

Figure 5.7 shows that NF_3 and Ar flows, followed by oxygen flow, have the most effect on the clean time indicated by the largest slope.

Based on the above investigation, the optimum clean time was achieved at 700 sccm of NF_3 diluted with 2300 sccm of Ar and 500 sccm of O_2. The chamber pressure should be kept around 2.7 Torr and the RF power around 450 Watt. Figure 5.7 shows that with these parameters the model predicts a clean time of 39 seconds. The summary fit of this model is shown in JMP Table 9. The proportion of variation explained by the model predicts an Rsquare of 93.57%.

Summary of Fit	
RSquare	0.935743
RSquare Adj	0.915662
Root Mean Square Error	4.171776
Mean of Response	50.14773
Observations (or Sum Wgts)	22

Table 9. Summary of the Clean Time model predicted By JMP Software.

5.1.6. Error Estimation

The baseline recipe shown above was run three times in order to determine the errors associated with the measurements. The 2-sigma standard of deviation was calculated in excel and found equal to 3.9 seconds.

5.2. Mass Balance

A fluorine mass balance was evaluated around the optimized clean recipe (700sccm NF_3, 2300sccm Ar, 500sccm O_2, 2.6 Torr, 450Watt) in order to estimate the destruction efficiency of NF_3 in the remote plasma and to quantify for the perfluorocompounds emitted from the CVD chamber. The optimized recipe was run five times (clean time =39 seconds) and the experimental errors (standard deviation) was determined.

5.2.1. Mass Balance with Optimized Clean Time

A full mass spectrum and absorbance spectrum were collected to determine the important peaks for analysis. Figure 5.8 displays the FTIR spectrum, which indicates the presence of SiF_4, CF_4, COF_2, HF, CO_2 and unreacted NF_3. In addition, F_2, N_2, O_2, and Ar were detected using Quadrupole Mass Spectroscopy (these gases do not have an infrared signature). A representative static mass spectrum is displayed in Figure 5.9.

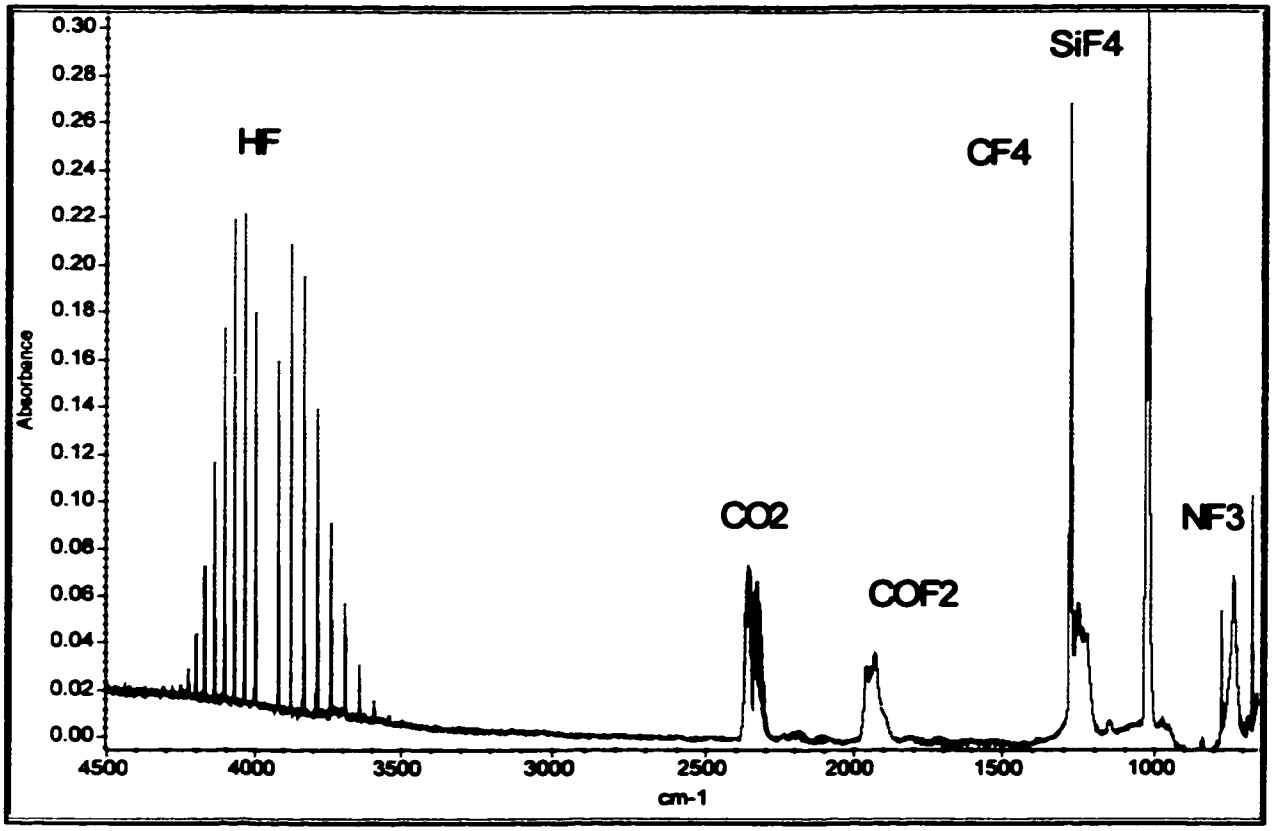


Figure 5.8. Typical FTIR spectrum recorded during the clean of Blok film.

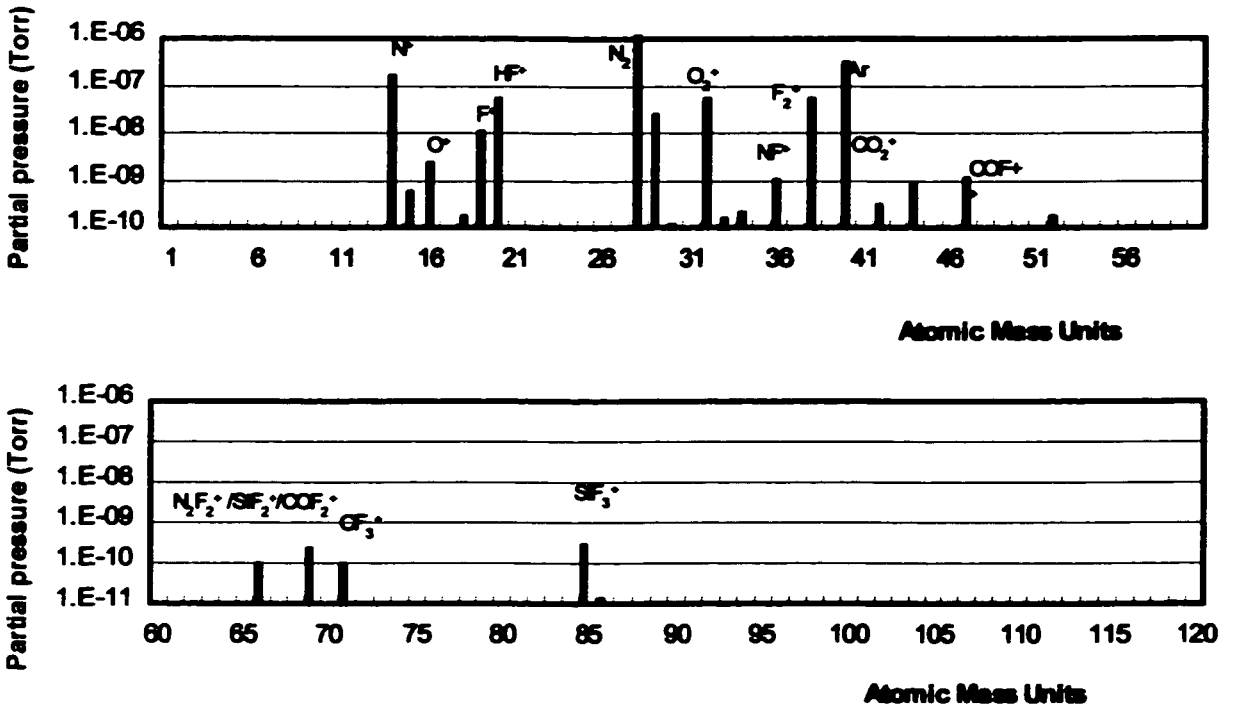


Figure 5.9. QMS Static spectrum recorded during Blok clean process.

The quantitative analysis, utilization efficiencies and kilograms of carbon equivalent (CE) recorded during the clean process are summarized in Table 10.

Emissions compound	Volume out (scc/clean)	equiv. outlet Halide	Mass out (1E-03gr /clean)	Utilization Efficiency (%)	Kg CE 100yrs (kg/10,000 wafers)	Kg CE infinite (kg/10,000 wafers)	vol.Clos (F) %
NF3 out	5.24	15.71	16.60	98.72	382.10	814.73	
SiF4	10.09	40.36	46.67				
F2	293.73	587.46	498.29				
CF4	9.47	37.87	37.20		659.38	86226.43	
COF2	99.16	198.32	292.17				
CO2	66.60	0.000	130.821		0.357	0.36	
HF	85.00	85.00	75.89				
NF3 in	408.33	1224.99	1294.26				
Overall	569.29	984.73	1097.83	98.72	1021.84	87041.51	78.75
Solid constitution	C	N	O	F	Si		
Molar %	36	3.7	6	50	4.4		

Table 10. Averaged Emissions during Blok Cleaning Process.

It was observed that the utilization removal efficiency of NF_3 was better than 98%. The Remote Clean technology ensures near-complete dissociation of the clean gas, and greatly reduces global warming emissions from the process, compared to classical *in-situ* clean processes. The clean process also generates global-warming CO_2 and CF_4, which are included in the overall kg CE calculation. It is interesting to note that the kg CE calculated over a 100 years horizon is dominated by both CF_4 and unreacted NF_3 emissions, (contribution of CO_2 is very small), while the kg CE calculated with an infinite time horizon is dominated by CF_4 emissions only. This is due to the much longer lifetime of CF_4 in the atmosphere (50,000 years), compared to NF_3 (740 years).

It is must be noted that the major byproduct of the clean process is molecular fluorine (F_2). These large amounts of F_2 emissions are due to recombination of atomic fluorine generated by the decomposition of NF_3. Not all F atoms react with the silicon containing compounds to form SiF_4, CF_4 and other byproducts but instead recombine to form F_2. Appropriate scrubbing techniques should be used to remove F_2 from the exhaust stream. The fluorine mass balance closed at only 78% suggesting that some fluorine-containing residues might have been formed in the foreline. A laboratory analysis of the foreline confirmed the existence of yellow residues. A summary of the analysis is included in table 10. Based on this laboratory analysis the mass of the solid formed in the foreline is estimated to 2.9 kilograms for every 10,000 wafers. The complete five wafer run are presented in Table 11.

Clean Number	Fluorine Volume closure
1	77.93%
2	77.37%
3	79.21%
4	76.65%
5	82.61%
Average	**78.75%**
Standard Deviation	**2.35%**

Table 11. Emissions Recorded during Blok Cleaning Process.

5.2.2. Mass Balance: Overetch Recipe

To fully clean the chamber from the residues, the clean time in the baseline recipe was increased by 25%. Figure 5.10 presents a time resolved QMS response during five process cleans of the Blok films.

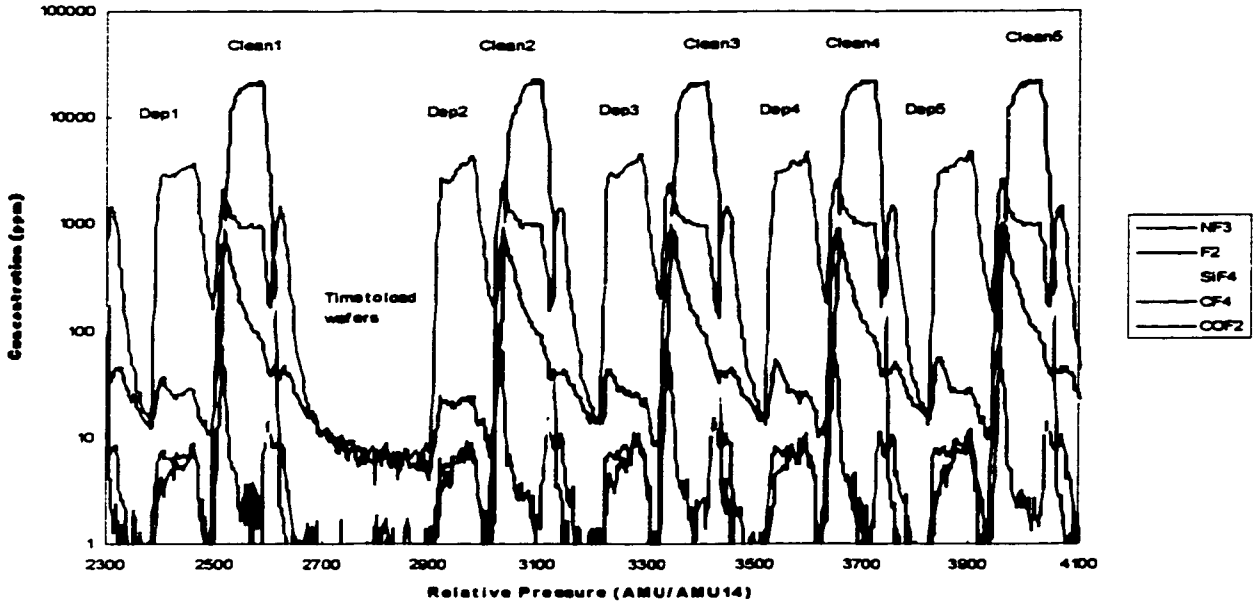


Figure 5.10. Time Resolved QMS Response during 5 Cleans of Blok Process.

It should be noted that during these process cleans SiF_4, CF_4, and COF_2 byproducts were present during the deposition step. This is due to reaction between TMS with F desorbing from chamber hardware. This fluorine was accounted for in the mass

balance. The quantitative analysis, NF_3 utilization efficiency, and kg CE of the PFCs recorded during this clean process are summarized in Tables 12 and 13.

Emissions compound	Volume out (scc/clean)	equiv. outlet Halide	Mass out (1E-03gr /clean)	Utilization Efficiency (%)	Kg CE (kg/10,000 wafers)	vol.Clos (F) %
NF3	1.46	4.38	4.63	99.84	100.97	
SiF4	39.83	159.33	184.93			
F2	1552.02	3104.03	2632.88			
CF4	33.35	133.39	131.01		2322.45	
COF2	153.46	306.92	452.16			
HF	201.60	201.60	180.00			
NF3 in	927.12	2781.36	2938.64			
Overall	1981.72	3909.65	3585.62	99.84	2423.42	115.84

Table 12. Averaged Emissions during Blok Cleaning Process with 25% Overetch.

Clean Number	Fluorine Volume closure (%)
1	116.25
2	108.4
3	116.29
4	119.60
5	118.69
Average	**115.84**
Standard Deviation	**4.44**

Table 13. Emissions during Blok Cleaning Process with 25% Overetch.

The NF_3 utilization efficiency is better than 99% confirming the efficiency of the RPS in totally breaking down NF_3 molecules. It was observed that the amount of SiF_4, CF_4, HF, and COF_2 formed during this clean process is higher than during the other recipe runs. Additional overetch time was obviously efficient in cleaning the chamber and preventing formation of particles that could contaminate the wafers during the deposition process.

The overall fluorine mass balance exceeds 100% (115%). At the beginning of this study, it was believed that this excess was likely due to an overvaluation of F_2 values reported, because the measured F_2 concentrations (~ 25,000ppm), as shown in Figure 5.11, are higher than the calibration range (maximum 10,000ppm). Therefore, an extrapolation was used to quantify F_2. This interpretation was excluded when a 5% F_2 concentration calibration was found linear and not much different from 1% calibration. The most probable explanation is first, due to the errors of the mass balance estimated to 11.44%, which include the experimental errors and the calibration errors. Second, the amount of fluorine that was absorbed by the walls before the clean process (during five runs that were designed to passivate the lines) cannot accounted for accurately. This fluorine desorbed from the chamber hardware during the deposition and clean processes.

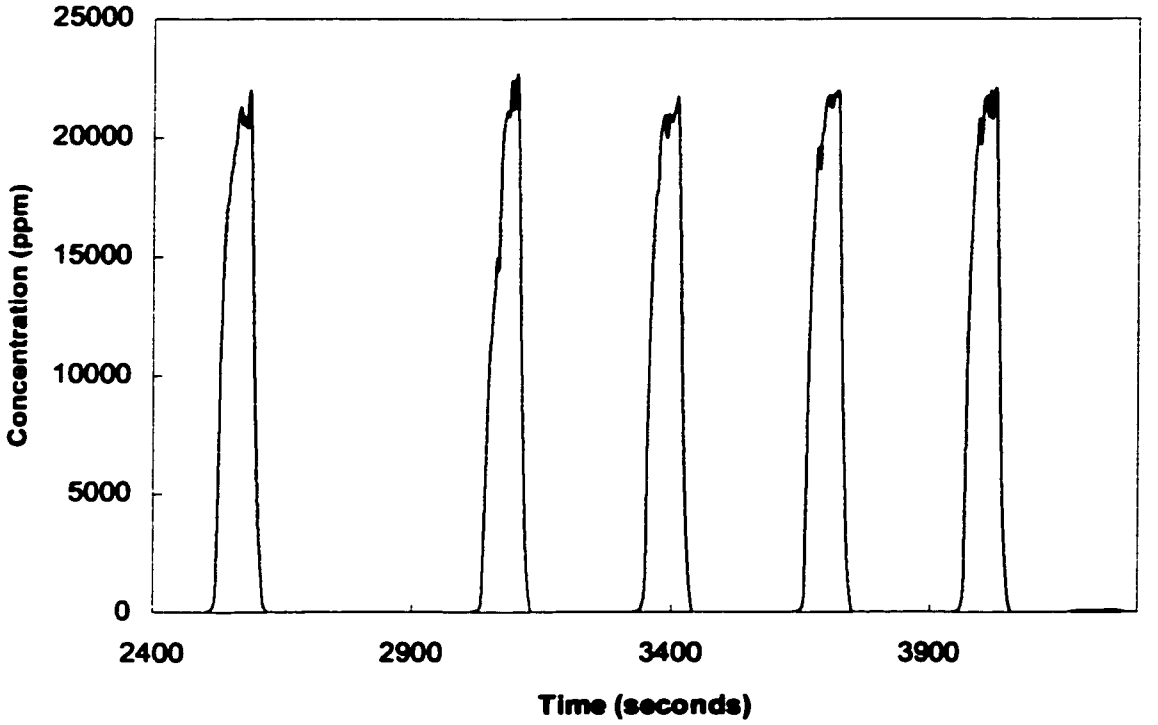


Figure 5.11. F_2 Evolution during Blok clean process.

5.3. PFC Emission Optimization by Design of Experiment

5.3.1. Response Surface Design

The effect of changing process variables on emissions was investigated by carrying a full matrix design of experiment (DOE). The parameters studied are the chamber pressure, the chamber RF power, NF_3 flow, and O_2 flow. These parameters were varied minus/plus 10% from the baseline values (700 NF_3, 500 O_2, 450W, 3.15Torr). The reactor baseline pressure of 2.7 Torr could not be kept constant for higher flows of NF_3 and O_2, therefore, this pressure was increased to 3.15 Torr. The total mass of emissions is presented in kg CE of PFC per 10,000 wafers which incorporate the global warming potential of the PFCs. CF_4 byproduct, unreacted NF_3, and CO_2 are the major global warming contributors. The data with the response column (PFC emission) is presented in Table 14.

Pattern	NF3(sccm)	O2(sccm)	RF(W)	P(Torr)	PFC (kgCE)
--00	630	450	450	3.15	3167
-+00	630	550	450	3.15	2806
+-00	770	450	450	3.15	2806
++00	770	550	450	3.15	2492
00--	700	500	405	3	2372
00-+	700	500	405	3.3	2512
00+-	700	500	495	3	2061
00++	700	500	495	3.3	2917
-00-	630	500	450	3	2701
-00+	630	500	450	3.3	2061
+00-	770	500	450	3	2266
+00+	770	500	450	3.3	3012
0--0	700	450	405	3.15	2176
0-+0	700	450	495	3.15	2503
0+-0	700	550	405	3.15	2703
0++0	700	550	495	3.15	3215
-0-0	630	500	405	3.15	2105
-0+0	630	500	495	3.15	2690
+0-0	770	500	405	3.15	2718
+0+0	770	500	495	3.15	2938
0-0-	700	450	450	3	2773
0-0+	700	450	450	3.3	2298
0+0-	700	550	450	3	2908
0+0+	700	550	450	3.3	2610
0000	700	500	450	3.15	2450
0000	700	500	450	3.15	2480
0000	700	500	450	3.15	2470

Table 14. JMP Table for a Four-factor Box-Behnken Design.

5.3.2. Screening for Interactions

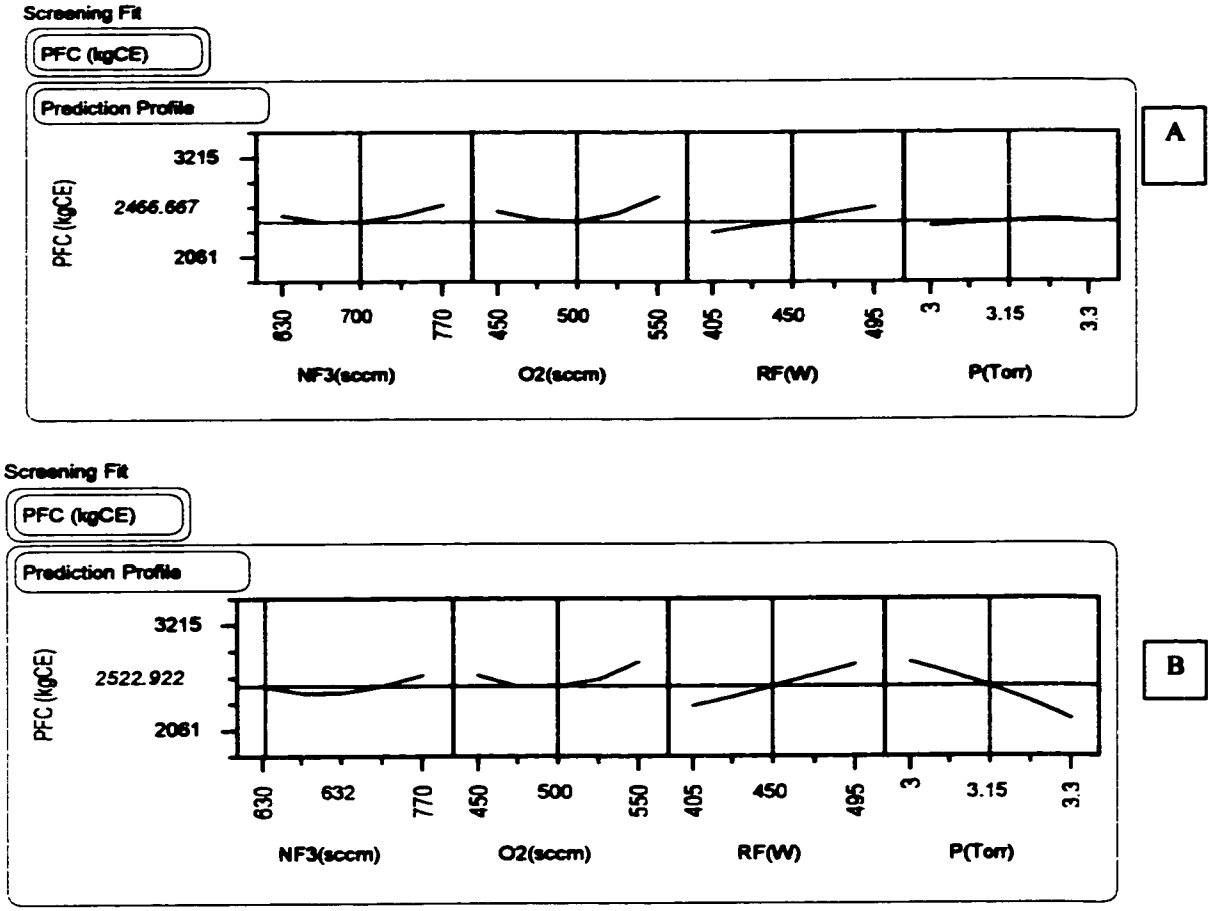


Figure 5.12. Fit Model dialog for PFC Emission.

The first glance at the resulting prediction profile plot in Figure 5.12.A shows that RF power has the most effect on the emissions of the PFCs, indeed, increasing RF power helps cleaning the chamber from carbon residues and making CF_4 as byproducts. The pressure plot is almost flat, suggesting that the chamber pressure does not have any effect on the PFCs formation. This could be true if there were no interactions between

parameters. The prediction profile plot at the bottom (Figure 5.12.B) shows responses when NF_3 flow is at its low setting and indicated by the vertical lines. The pressure's slope changed dramatically which indicates an interaction between NF_3 flow and the pressure in the chamber. When there is no interaction, only the heights of the profile would change not the slope. Interaction plots between all the parameters are shown in figure 5.13.

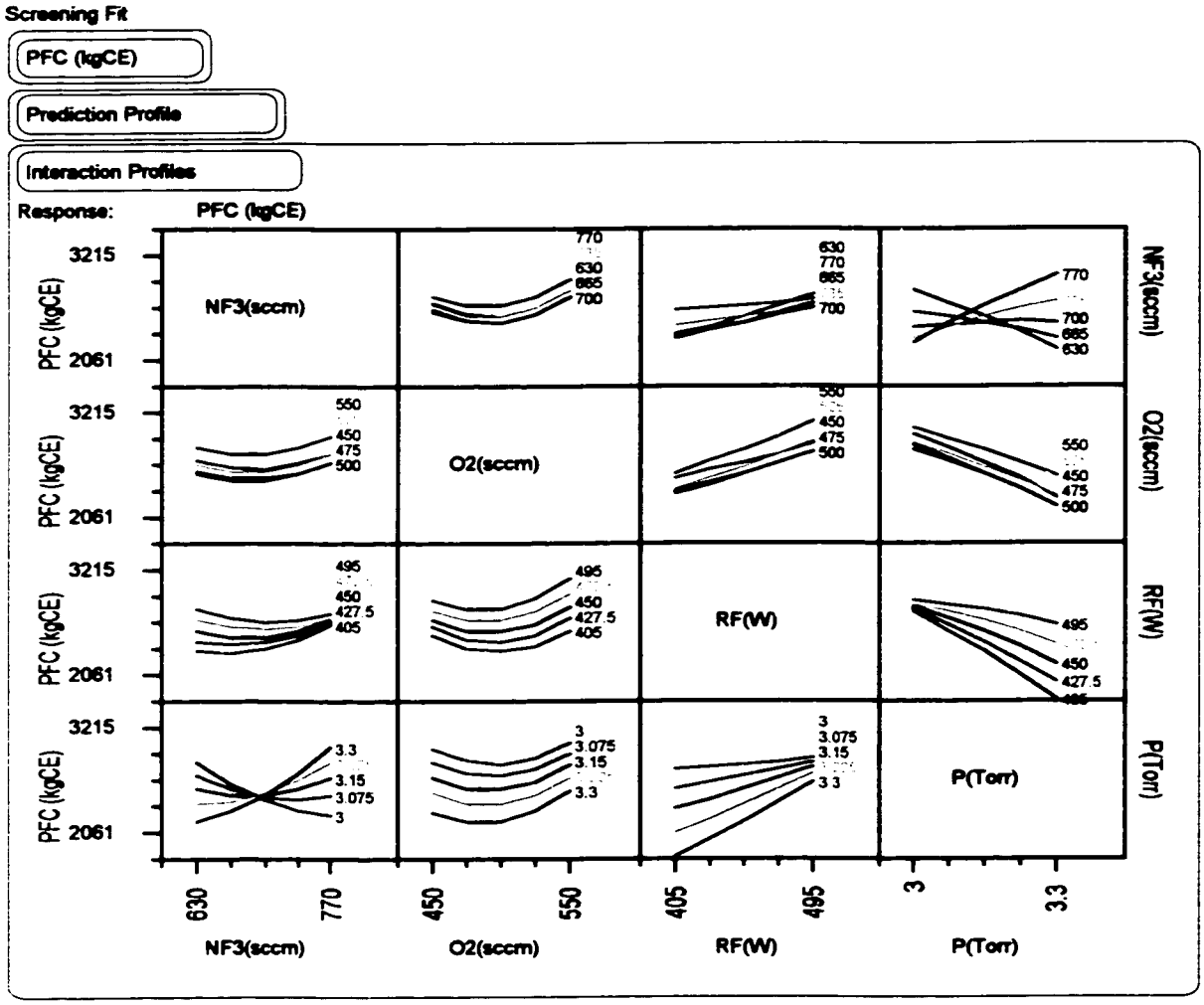


Figure 5.13. Interaction Plots for four Factors PFC Emission Experiment.

Each small plot in Figure 5.13 shows the effect of two factors on the response. One factor (associated with the column of the matrix of plots) is on the X axis. This factor's effect shows as the slope of the lines in the plot. The other factor becomes multiple prediction profiles as it varies from low to high. This factor shows its effect on the response as the vertical separation of the profile lines. If there is an interaction, then the slopes are different for different profile lines, like those in the P by NF_3 plot.

The interaction between the other parameters is not significant as shown in Figure 5.12 A&B, where the change in the NF_3 value didn't affect significantly the slope of the other parameters except the pressure. This is confirmed in Table 15, which shows the probability of getting these estimations by chance alone. The interaction between the pressure and NF_3 has a 5% probability that is due to the chance alone, whereas, the other interactions have larger probability.

Term	Prob>|t|
NF3(sccm*NF3(sccm	41.42%
O2(sccm)*NF3(sccm	94.39%
O2(sccm)*O2(sccm)	17.02%
RF(W)*NF3(sccm	58.73%
RF(W)*O2(sccm)	78.22%
RF(W)*RF(W)	92.66%
P(Torr)*NF3(sccm	5.57%
P(Torr)*O2(sccm)	79.14%
P(Torr)*RF(W)	29.54%
P(Torr)*P(Torr)	78.76%

Table 15. Significant probability of the Parameters Interactions.

The effect of the pressure on the PFC emissions is shown in Figure 5.14. The cube plots show that at low pressures (3 Torr), an increase in NF_3 flow from 630 to 770 sccm results in 14 to 26% decrease in the PFCs emissions. At higher pressure (3.3 Torr), increasing the NF_3 flow results in increasing the PFCs formation. This is probably due to the fact that at high pressure some of the dissociated NF_3 is recombined.

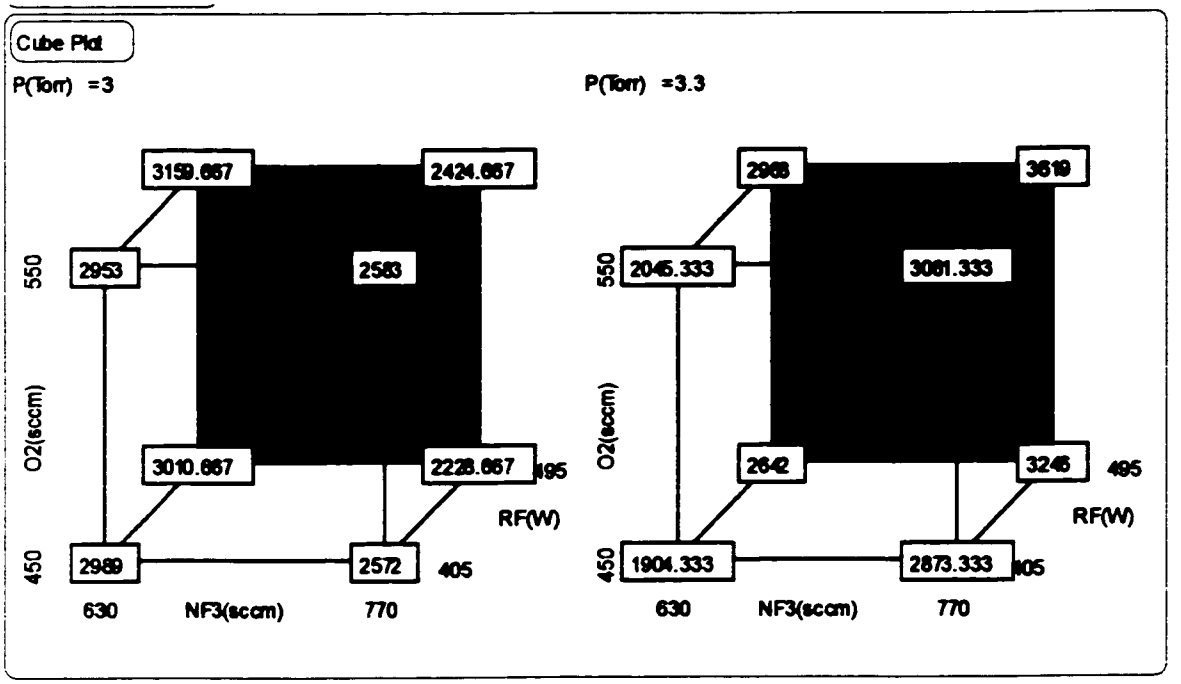


Figure 5.14. Cube Plots of the PFCs Emissiosns.

5.3.3. Optimum Solution

Table 16 indicates the critical values of the surface and the kind of solution (maximum, minimum, or saddlepoint) expected.

Solution

Variable	Critical Value
NF3(sccm)	716.49313
O2(sccm)	497.08557
RF(W)	412.44277
P(Torr)	3.0675575
Solution is a	SaddlePoint
Predicted Value at Solution	2403.1294

Table 16. Response Surface Critical Value.

The critical values presented in Table 16 are the optimum values where the surface has a slope of zero, this corresponds to PFCs emissions of 2.4 Tons per 10,000 wafers. Figure 5.15 shows the surface response for the saddle point solution. Based on this information JMP software predicts an equation model of the form:

$$\textbf{PFCs emissions} = 1.3 * 10^{-5} - (126 * NF_3) - (111.18 * O_2) - (76.24 * RF) - (26869 * P) + (0.024 * NF_3^2) + (0.083 * O_2^2) - (0.029 * RF * NF_3) + (33 * P * NF_3) + (26.52 * P * RF).$$

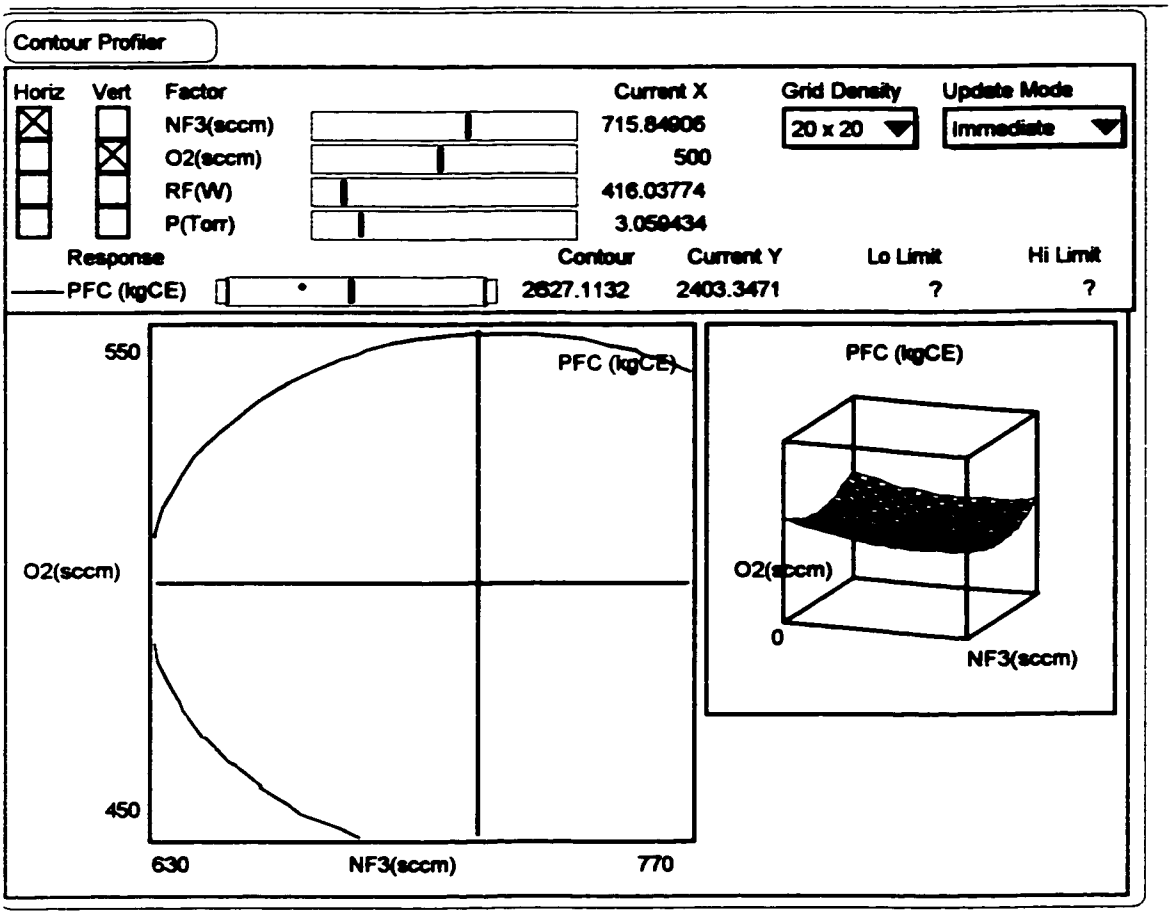


Figure 5.15. Surface Response of the PFC emission DOE.

Chapter 6

Conclusions

The remote plasma technology was evaluated for cleaning a silicon carbide film on a PECVD chamber. The clean time and PFC emissions were monitored using a quadrupole mass spectroscopy and Fourier Transform Infrared spectroscopy. From the data presented in this study, it can be concluded that:

1) Increasing NF_3 flow improves significantly the chamber clean time due to higher fluorine radicals available to clean the chamber.

2) Addition of Ar prevents the recombination of fluorine radicals to molecular fluorine and improves the clean time.

3) Addition of oxygen and in-situ RF power helps removing the carbon from Blok residues. Oxygen also minimizes the formation of global warming CF_4 and instead forms COF_2 and CO_2.

4) The optimum clean time is achieved with 2300 sccm NF_3 diluted with 2300 sccm Ar and 500 sccm O_2. RF power of 450 W is necessary to enhance the clean rate and the pressure in the chamber should be kept to its minimum.

5) With 39 seconds clean time, the fluorine mass balance closed at only 78% suggesting that solid particles were formed in the foreline. This was confirmed by a laboratory analysis of the residues in the chamber. When a 25% overetch time was added to the

clean time recipe, the mass balance improved, hence reducing the amount of particles that could contaminate the wafer during deposition.

6) The fluorine desorbing from the chamber hardware can significantly increase the mass balance and biased the results. A mass balance in a clean chamber (run the clean recipe without deposition process) should be performed prior starting the tests in order to determine the amount of fluorine that is absorbed by the chamber hardware.

7) Based on the DOE performed to model the PFCs emissions, the pressure significantly interacts with NF_3 and can influence the PFCs emission trends. The 10% DOE variation of O_2 was not sufficient to significantly affect PFCs emissions. The optimum variables were found for 716 sccm NF_3, 497 O_2, 412 Watt, and 3.06 Torr. This recipe not very different from the center point recipe previously optimized.

8) The optimized recipe for Blok film emits 2400 Kg CE of PFCs. This value is not significant when it is compared with PFC in-situ cleans. An oxide or nitride C_2F_6 in-situ clean process emits 25 times this amount (Raoux et al., 1999). NF_3 remote plasma reduces significantly the global warming gas emissions.

Chapter 7

Future Research

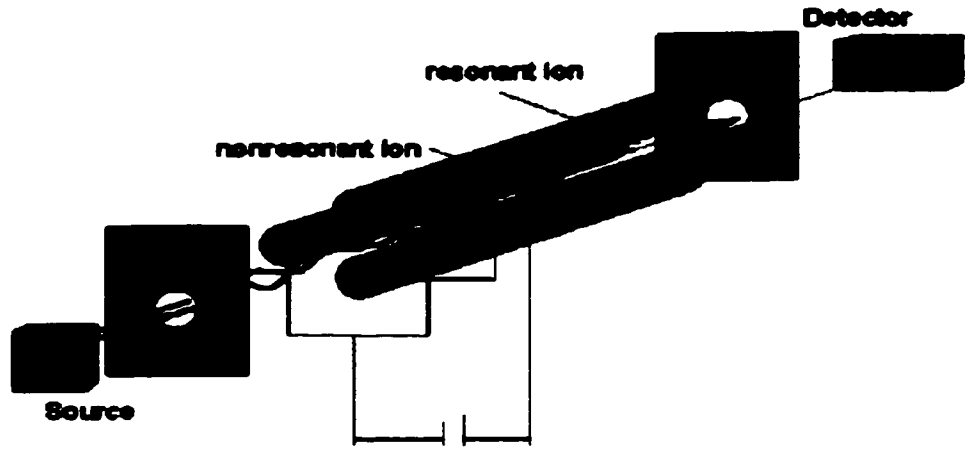
The remote clean plasmas using NF_3 overcome many of the challenges related to the recombination of the PFC clean gas and its emission to the atmosphere. The NF_3 utilization efficiency of more than 98% dramatically reduces the amount of kg CE emitted into the atmosphere compared to traditional PFC in-situ cleans. However, there are some issues that compromise the benefits of utilizing NF_3 remote plasma cleans. For instance, it was shown in Chapter 5 that the major byproduct of NF_3 RPS cleans is molecular fluorine. Post treatment is required to dispose of these species, which means adding additional cost for the inefficiency of the process and optimization of the process has its limitation in reducing the amount of F_2 formed. Therefore, further research is necessary to increase the efficiency of the clean in the chamber by modifying the flow path and materials used from the remote source to the chamber in order to minimize fluorine recombination. Another issue is related to the shortage of NF_3 supplies, which inflates the price of the gas and has given rise to high gas cost per wafer. Research should be conducted to find alternative lower cost cleaning gas.

APPENDIX A

Theory of the Quadrupole Mass Spectrometer

Mass spectrometry is an analytical technique for the identification of ions by way of measuring their mass-to-charge, m/e, ratios. The sampling and flow of the gas sample is accomplished by successive reduction of pressure from the process to the compound pump through fixed geometry pump-in-channels.

A quadrupole mass spectrometer is made up of three distinct parts: the ion source, the quadrupole mass filter, and the ion detector (Figure A1).



A.1 : Mass spectrometer components.

Ion source

Inside the ion source, a heated filament emits electrons, which bombard the incoming gas molecules, giving them an electrical charge. The filament is a tungsten wire that can resist to aggressive gases, particularly those containing fluorine and chlorine. The filament is heated with a DC current from the emission regulator circuit, with the resulting temperature of the filament used as the means of controlling the emission current.

The filament is centered over a hole in the anode cylinder. The voltage on the anode is positive with respect to the filament. The electron repeller is located behind the filament and is electrically connected to the negative side of the filament. The potential difference between the filament and the anode determines the kinetic energy (also called electron energy) of the emitted electrons. The electron energy determines how gas molecules will ionize when struck by the electrons.

Quadrupole mass filter

The ions produced in the ion source are injected into the mass filter, which rejects all ions except those of a specific mass-to-charge ratio. A combination of RF and DC potentials is applied to the quadrupole. The RF frequency and amplitude determine the mass, and the RF/DC ratio determines the filter selectivity. The mass filter's four rods are alternately charged to direct ions of specific masses down through the center, deflecting all larger and smaller masses.

The RF component removes the low-mass ions from the beam. Ions of sufficiently low mass have their motions remain in phase with that of the applied RF.

These ions will gain energy from the field and oscillate with increasingly large amplitudes. Eventually, as they travel along the length of the rods, they will strike one of the rods and are neutralized.

The DC component is superimposed on the RF to remove high-mass ions from the beam. The DC field deflects the high-mass ions toward the negative poles, opposing the effects of the RF field. Eventually, these high mass ions strike the negative rods and are neutralized.

The mass of the ions passed by the filter is determined by the RF amplitude, the RF frequency, and the quadrupole radius , as shown by the following equation: $V = 14.438*M*f^2*r^2$, V is the RF amplitude in Volts, M is the mass of the ion in atomic mass units (AMU) per electron charge, f is the RF frequency in megahertz, and r is the quadrupole radius in centimeters.

Ion detector

The ion detector consists on an electron multiplier (EM) and a Faraday cup (FC). When an ion strikes the surface of the EM, one or more secondary electrons are emitted. These electrons are accelerated to a second surface which is at a more positive potential, where additional electrons are generated. This process repeats itself until a pulse of electrons emerges from the output of the EM and is collected on a Faraday cup. The result is that as many as a million electrons or more can be produced by each ion.

The advantage of the EM detector sensor is its high sensitivity (as much as 100 amps /Torr), making it possible to measure partial pressures as low as $2*10^{-12}$ Torr.

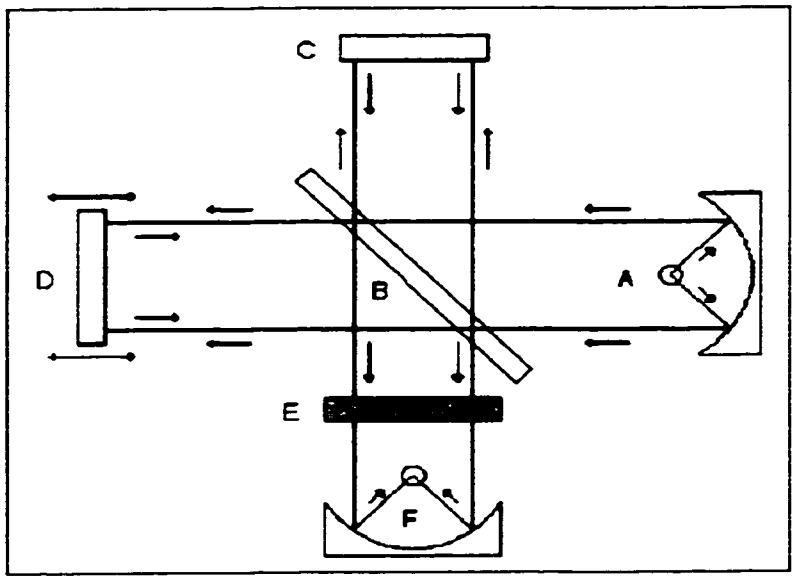
APPENDIX B

Theory of Fourier transform infrared

Infrared spectroscopy is a study of the interaction of matter with infrared radiation. Infrared (IR) radiation is electromagnetic radiation that encompasses all the wavelengths between visible and microwave regions of the electromagnetic spectrum. The infrared is divided into three regions, according to the different types of atomic and molecular energy levels. Radiation in the near-infrared at 4000-12500 cm^{-1} can excite harmonics of molecular vibrations as well as low-energy electronic transitions in molecules and crystals. The mid-infrared region at 200-4000 cm^{-1} is where most stretching and bending vibrations of molecules occur. The far-infrared region at 10-200 cm^{-1} is where rotational transitions in gaseous molecules, low-frequency bending, torsional and skeletal vibrations are observed.

Fourier transform infrared (FTIR)

The components of an FTIR spectrometer are shown in the figure below.



B1: Sketch of FTIR components.

Radiation from the source A is divided in the beam splitter B. This beam splitter, made from an infrared transparent material such as KBr, sends half of the beam to a fixed mirror C and half to a moving mirror D. Upon reflection from the moving mirror, radiation is then directed back to the splitter. At the beam splitter some of the light that has been reflected from the fixed mirror combines with light reflected from the moving mirror and is directed towards the sample. After passing through sample E the radiation is focused onto the detector F. The interferogram is scanned by moving D from zero path

difference to some distance L_{max}; it is then Fourier-transformed and displayed as a spectrum on the recorder.

Spectra

Infrared spectra are usually plotted as percent transmittance T or absorbance A on a scale linear in wave number ν. Transmittance is the ratio of the intensity of radiation transmitted by the sample (I) to that incident on the sample (I_0), expressed as a percentage:

$$A = \log_{10} (I_0/I) = \log_{10} (100/T) \qquad \text{(B1)}$$

Applications

Among the more important applications of the FTIR are chemical analysis and the determination of molecular structures. FTIR is ideal for identifying chemical compounds because every molecule, except homonuclear diatomics such as nitrogen (N_2), oxygen (O_2), and fluorine (F_2), has an infrared spectrum. Since the vibrational frequencies depend upon the masses of the constituent atoms and the strengths and geometry of the chemical bonds, the spectrum of every molecule is unique (except for optical isomers). Pure unknowns cab thus be identified by comparing their spectra with recorded spectra.

Quantitative infrared analysis is possible because as defined in equation B1 is directly proportional to the number of absorbing molecules, and in mixtures is the sum of the absorbances of the individual components. The Beer-Lambert law is given in equation B2:

$$A(\nu) = a(\nu)bc \qquad \text{(B2)}$$

Where a, b, and c are the absorptivity, path length , and concentration respectively. When the absorptivity of a compound is known at a given frequency, at an absorption peak, the concentration of that compound in a mixture can be determined from equation 2.

APPENDIX C

QMS and FTIR Calibrations

For NF_3, F_2, CF_4,HF, COF_2 and SiF_4 calibration curves were obtained by dilution of gas standards (1vol% in N_2 carrier) with pure N_2 gas. Table C1 summarizes the IR absorption bands or selected AMUs for the different species detected during the measurements. The methods used to quantify emissions are also indicated.

Species	CO2	CF4	COF2	SiF_4	NF_3	F_2	HF
IR region (cm^{-1})	2360						~4038
QMS(amu)		69	47	85	52	38	
Quant. method	FTIR	QMS	QMS	QMS	QMS	QMS	FTIR

Table C.1 – Summary of effluent species and detection methodology.

In order to provide accurate quantitative data, an NF_3 calibration and a rare-gas (1% He, Ne, Ar, Xe, Kr in N_2) calibration was performed every day (before and after the deposition / clean measurements). This allows accounting for the day-to-day variation of the QMS sensitivity. F_2 calibration was performed on the last day of the experiment. The FTIR sensitivity was checked during the NF_3 calibration, but the stability of the FTIR method did not require daily calibration.

CO2 Calibration (2360 cm^{-1} IR region):

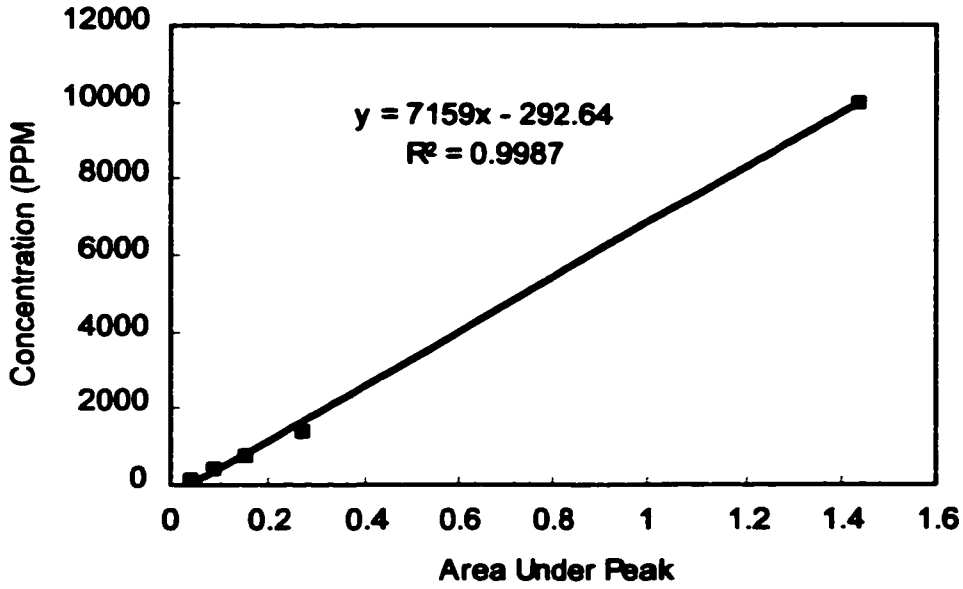


Figure C.1 – Carbon dioxide calibration curve obtained with FTIR.

SiF_4 Calibration :

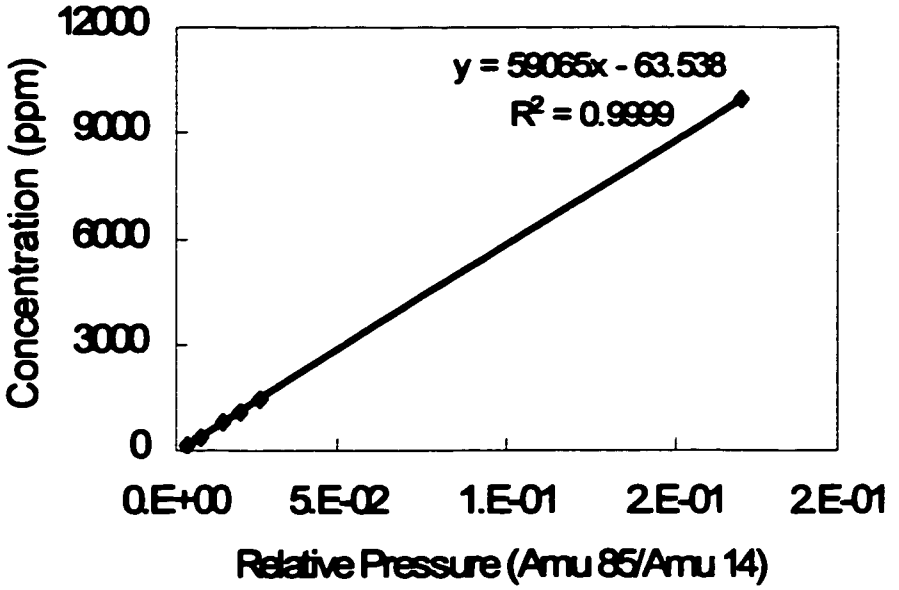


Figure C.2 – Silicon tetrafluoride calibration curve obtained with QMS (AMU85).

NF_3 Calibration:

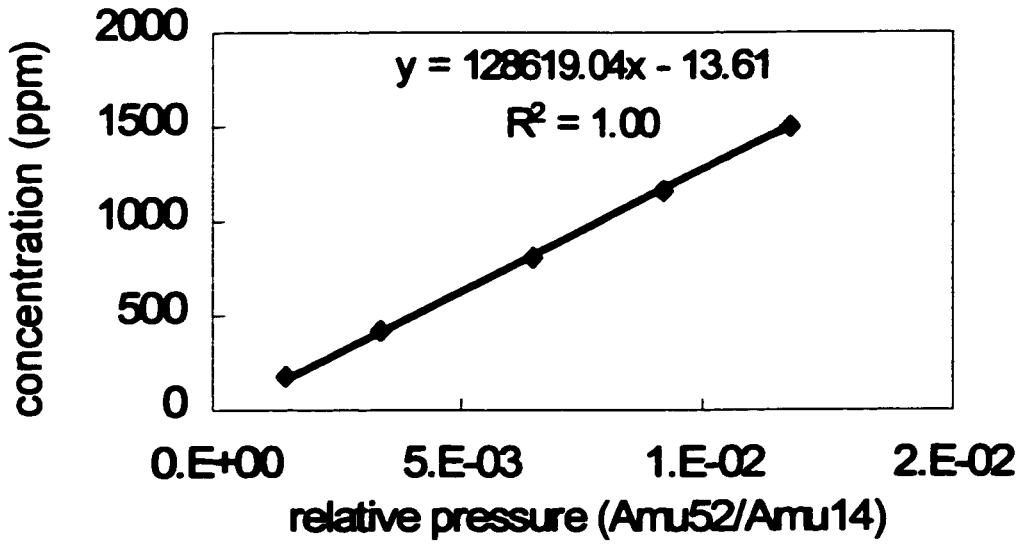


Figure C.3 –Nitrogen trifluoride calibration curve obtained with QMS (AMU 52).

F_2 Calibration :

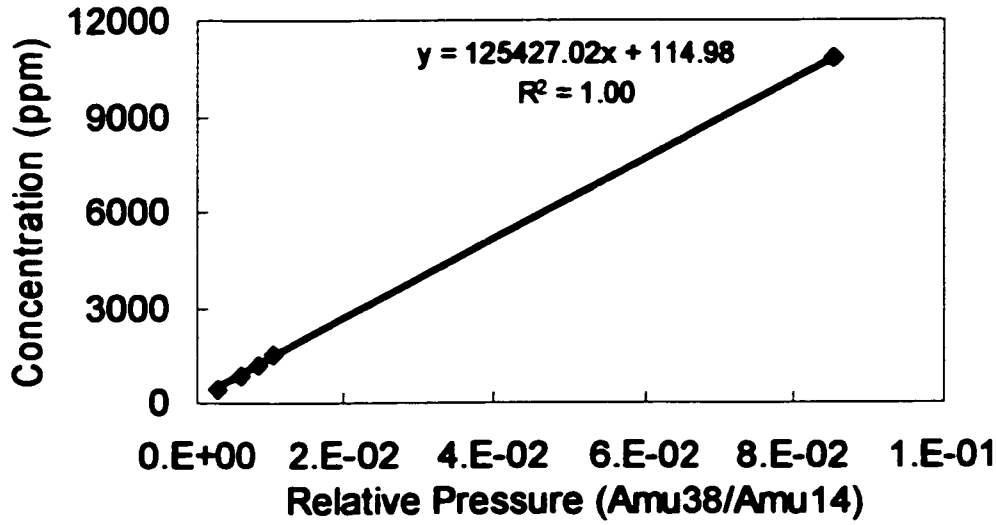


Figure C.4 –Fluorine calibration curve obtained with QMS (AMU 38).

CF_4 Calibration:

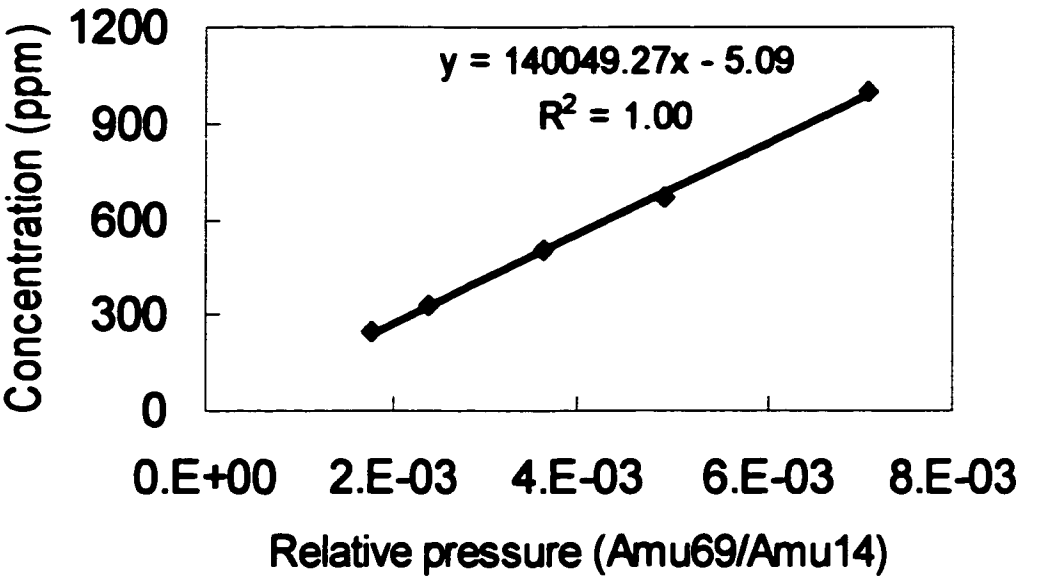


Figure C.5 –Carbon tetrafluoride calibration curve obtained with QMS (AMU 59).

COF_2 Calibration :

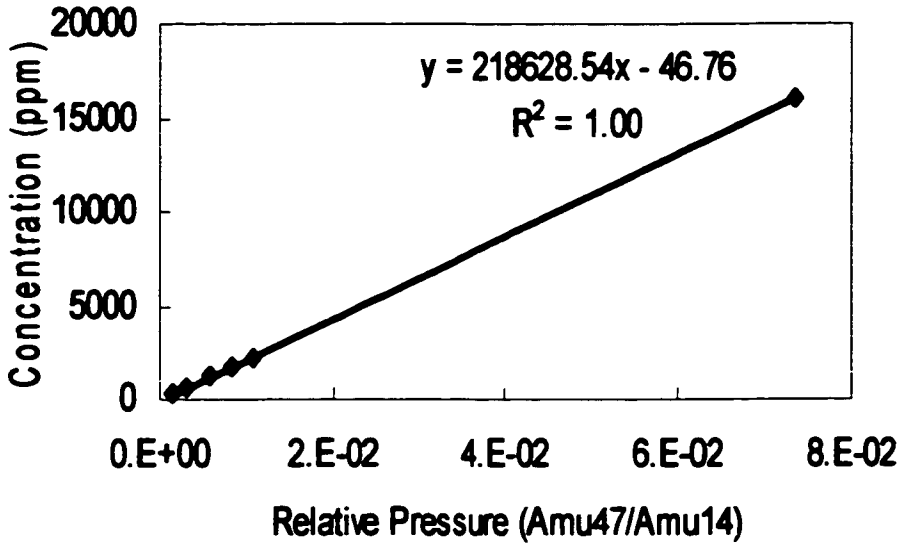


Figure C.6 –Carbonyl fluoride calibration curve obtained with QMS (AMU 47).

HF Calibration:

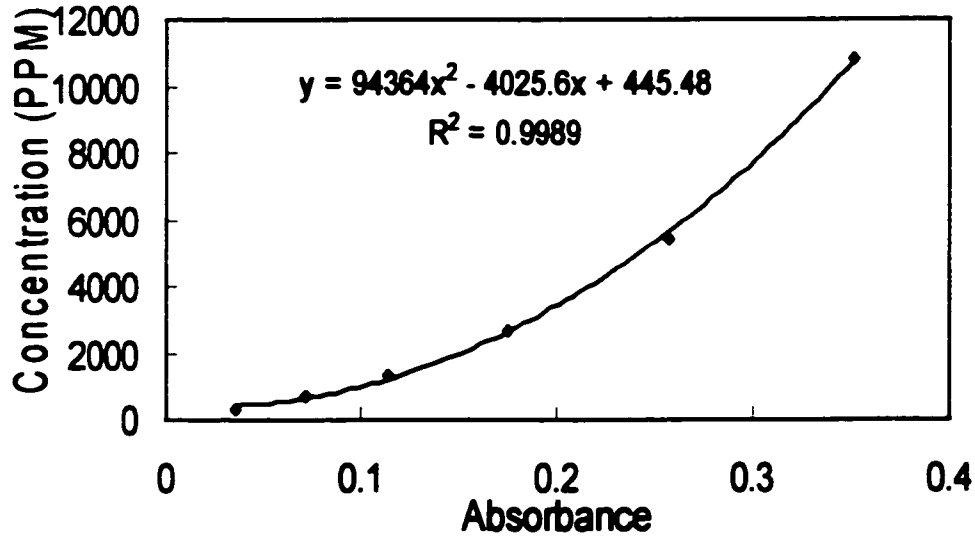


Figure C.7 – Hydrogen fluoride calibration curve obtained with FTIR.

REFERENCES

Box, G., Hunter, W., Hunter, J. *Statistics for Experimenters*. 1978. John Wiley & sons, Inc. USA.

Dupont. 2000. *PFC Emissions Reduction from Semiconductor Processing Tools: Eighth Status Report on Technology and Industry Activities.* January 2000. http://www.dupont.com/zyron/techinfo/status8.html.

Emissions Measurements and Technology, Applied materials, 1999.

EPA. 2000. *Draft Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-1998.* Office of Policy, Planning, and Evaluation, U.S. Environmental Protection Agency, Washington, DC; EPA 236-R-99-003. http://www.epa.gov/globalwarming/emissions/national/download.html.

International SEMATECH. 1999. *Motorola Evaluation of the Applied Science and Technology, Inc. (ASTex) ASTRON Technology for perfluorocompound (PFC) Emissions Reductions on the Applied Materials DxL Chemical Vapor Deposition (CVD) Chamber.* Presented at: A Partnership for PFC Emissions Reductions, October 18, 1999, Semicon Southwest 99. Austin, Texas.

Kelly, R. 1999. *Praxair's PFC Capture Technology*. Praxair Inc. Presented at: A Partnership for PFC Emissions Reductions, October 18, 1999, Semicon Southwest 99. Austin, Texas.

Ketkar, S., Scott, A., Martinez de Pinillos, J. 1994. Dynamic Dilution Calibration System for Calibrating Analytical Instruments Used in Gas Analysis. J. Electrochemical Society, 141-184 (1994).

Lieberman, M., Lichtenberg, A. 1994. *Principles of Plasma Discharges and Materials Processing*. John Wiley & Sons, Inc,.

Meyers, J. *Equipment Environmental Characterization Guidelines*. Intel Corporation. Revision 3.0.

Mocella, M. 1998. *PFC Recovery: Issues, Technologies, and Considerations for Post-Recovery Processing*. Dupont Flouroproducts, Zyron Electron Gases Group.

Pruette, L., Karecki, S., Reif, R., Langan, J., Rogers, S. 1998. *Evaluation of Trifluoroacetic Anhydride as an Alternative PECVD Chamber Clean Chemistry*. Journal of Vacuum Science Technology, May/June 1998.

Raoux, S., Langan, J. 1999. *Remote NF_3 Chamber Clean Virtually eliminates PFC Emissions from CVD Chambers and Improves System Productivity*. Semiconductor Fabtech – 9th Edition.

Raoux, S., Tanaka, T. 1999. *Remote microwave plasma source for cleaning CVD chambers*. Journal of Vacuum Society, B17(2), Mar/Apr 1999.

Shang, Q. 1999. *Design Review: Remote microwave source at AKT*. ET Working Group on Plasma Sources.

Sun, P., Benett, D., Zazzera, L., Reagen, W. 1998. *Reducing PFC emissions using C_3F_8 – based PECVD clean*. Semiconductor International, February 1998.